

Air



Rubber Products Styrene-Butadiene Rubber Manufacture

Emission Test Report General Tire and Rubber Company Mogadore Chemical Plant Mogadore, Ohio

SOURCE TEST AT GENERAL TIRE'S
STYRENE BUTADIENE RUBBER PLANT

Mogadore, Ohio

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Technical Manager: Terry Harrison

Prepared for:

United States Environmental Protection Agency
Emission Standards and Engineering Division
Emission Measurement Branch
Research Triangle Park, North Carolina 27711

By:

TRW

ENVIRONMENTAL ENGINEERING DIVISION

Post Office Box 13000
Research Triangle Park, North Carolina 22209

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GLOSSARY OF TERMS

| | | |
|---------|---|---|
| EMB | - | Emission Measurement Branch |
| EPA | - | Environmental Protection Agency |
| SBR | - | Styrene/Butadiene Rubber |
| VOC | - | Volatile Organic Compounds |
| NSPS | - | New Source Performance Standards |
| NESHAPS | - | National Emission Standards For Hazardous Pollutants |
| CVS | - | Central Vacuum System |
| FID | - | Flame Ionization Detector |
| GC | - | Gas Chromatograph |
| TC | - | Thermal Conductivity |
| ppm | - | parts per million |
| Rx | - | Reactor |
| GPM | - | Gallons Per Minute |
| BDT | - | Blowdown Tank |
| SSS | - | Styrene Stripper System |
| PST | - | Product Storage Tank |
| ss | - | Shaker Screens |
| E_D | - | Equivalent Diameters |
| D_p | - | Differential pressure |
| psi | - | pounds per square inch |
| QA | - | Quality Assurance |
| TBC | - | 4-tertiary Butylcatechol/4-tertiary Butylpyrocatechol |
| SD | - | Standard Deviation |
| MeCl | - | Methylene Chloride |

SAMPLE POINT IDENTIFICATION KEY

| <u>Point</u> | <u>Sample Identification</u> |
|--------------|--|
| 1A | Reactor/Blowdown Tank (BDT-4) Exhaust |
| 1 | Central Vacuum System (CVS) Exhaust |
| 2 | Styrene Stripper Vacuum System Exhaust |
| 3 | Shaker Screens Exhaust |
| 4 | Blowdown Tank Inlet Latex Stream |
| 5 | Blowdown Tank Outlet Latex Stream |
| 8 | Styrene Stripper Inlet Latex Stream |
| 9 | Styrene Stripper Outlet Latex Stream |
| 11 | Product Storage Tank Vent |

1. INTRODUCTION

Under the supervision of the Emissions Measurement Branch (EMB) of the Environmental Protection Agency (EPA), TRW Environmental Engineering Division personnel conducted a study of the volatile organic emissions produced by the Styrene/Butadiene Rubber (SBR) Industry at General Tire's facility in Mogadore, Ohio.

Information obtained from the February 4, 1980 presurvey of the plant in Mogadore was used to develop a test plan. The field sampling and analysis was performed from March 24 through April 4, 1980.

The purposes of this test were: 1) to determine the total volatile organic emissions of the plant; 2) to study the mass balance of styrene around the blowdown tank and styrene stripper; 3) to obtain data concerning the VOC emissions to provide design criteria for possible control devices; and 4) to determine the degradation rates of organic compounds in the gas and latex samples. The specific compounds under analysis include: butadiene, benzene, toluene, ethylbenzene, xylenes, styrene, CO_2 , O_2 , and N_2 . The sampling points are described in Section 5; with the sampling and analytical preparations and procedures being described in Section 6.

This information was collected and may be used in the development of possible New Source Performance Standards (NSPS), the National Emission Standards for Hazardous Pollutants (NESHAPS).

2. SUMMARY

The latex produced at the General Tire plant in Mogadore, Ohio, was a butadiene specialty latex. This project studies the residual styrene and butadiene emissions resulting from the formation of SBR. The testing encompassed a two-week period. The first week involved sampling and analysis of the blowdown system. The second week involved sampling of the styrene stripper system, shaker screens, and storage tank. For a clear understanding of the summary discussion, the plant process must be understood (Section 4). A brief overview of the plant and the process are described below.

2.1 PLANT PROCESS SUMMARY (Figure 2-1)

The latex is prepared in a reactor from raw materials. When the latex in three reactors reached completion the contents were emptied into a blowdown tank. The emissions from filling the blowdown tank were channeled through a condenser and vented through the central vacuum system. The latex left the blowdown tank system and was filtered through a vibrating screen which removed any congealed latex. The screens were open to the atmosphere inside the building, and a gas sample was collected at this location. The latex then flowed into a large pre-blend tank for storage. When needed, the latex was transferred to the steam stripper for removal of the remaining residual styrene and other hydrocarbons. The emissions generated by this process were vented through the steam stripper vacuum system. Samples of these gaseous emissions were collected along with samples of the latex before and after steam stripping. If further product treatments were required, the latex was routed to the blend tank. Otherwise, the finished latex product was transferred to the product storage tank. A vent on the storage tank permitted gas sampling data collection.

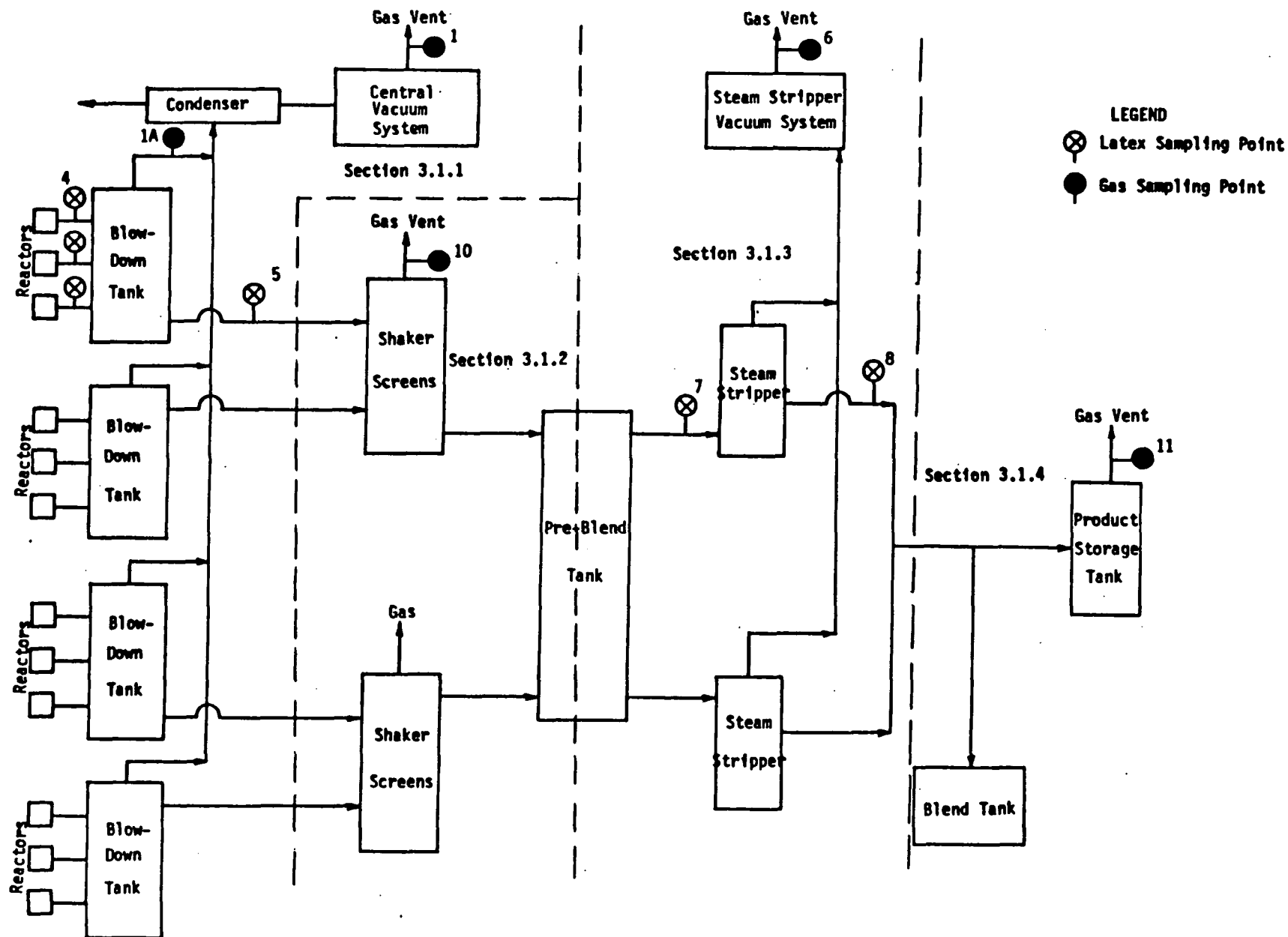


Figure 2-1. Styrene/Butadiene Rubber Process

2.2 RESULTS SUMMARY

The objectives for the test included: 1) the quantification of volatile organic emissions produced by normal process operation (Section 2.2.1); 2) measurement and characterization of emissions produced from a reactor dump prior to treatment by the control device (Section 2.2.2); and 3) the determination of a material balance of residual styrene between the blowdown tank and the steam stripper (Section 2.2.3).

2.2.1. Volatile Organic Compound (VOC) Emissions

The summary Table 2-1 lists the average hydrocarbon emissions and flow data from the test period. The results from the blowdown outlet on the table are not VOC emission results, because the emissions were not directly vented to the atmosphere, and will be discussed in a later section. The results from the central vacuum system are VOC emission results and include the hydrocarbon concentrations from the condensate collected in the gas stream. They represent the average of a total reactor dump-degassing cycle. However, there were other processes in the plant that vented through the central vacuum system so that the totals do not necessarily represent only the blowdown of the reactors studied. The cycle lasted approximately 8 hours, during which time the temperatures and emission concentrations varied from the average considerably. The results from each test are discussed separately in Section 3.

The results from the shaker screen are expressed in concentration units only because no flow measurements could be made. The results indicate very low levels of hydrocarbon emissions from the shaker screens.

The results from the steam stripper are the average emissions collected from the vent during an 8-hour period. The individual tests (Section 3) were consistent so that the averages are representative of the emissions associated with the operating process. The results from the storage tank are the average emissions collected from the vent during an 8-hour period. The individual tests (Section 3) were

Table 2-1. SUMMARY OF AVERAGE GASEOUS EMISSION RESULTS
FROM THE TEST LOCATIONS AT THE GENERAL TIRE
FACILITY IN MOGADORE, OHIO

| | Blowdown outlet ^{a,g} | Central vacuum system ^{b,g} | Steam stripper outlet ^c | Storage tank outlet ^c | Shaker screen ^d |
|--|--------------------------------|--------------------------------------|------------------------------------|----------------------------------|----------------------------|
| Process Data | | | | | |
| Flue gas temperature (°F) | 151 | 112 | 60 | 91 | 103 |
| Flue gas area (ft ²) | f | 0.087 | 0.09 | 0.087 | NA |
| Flow rate (SCFM) | 111.98 | 105.13 | 7.51 | 6.38 | NA |
| Vacuum pressure (in.Hg) Absolute | 12.7 | 30.8 | 29.0 | 29.0 | 29.0 |
| Emission rate (lb/hr) | 55.2 | 64.3 | 1.2 | 0.20 | 10 |
| Analytical Results^a (ppmv as compound) | | | | | |
| 1. Butadiene | 128,881 | 54,758 | 361 | 55.8 | 39.2 |
| 2. Benzene | 61.6 | 23.4 | 2.91 | 0 | 0 |
| 3. Toluene | 231 | 15.3 | 12.9 | 40.0 | 0 |
| 4. Ethylbenzene | 432 | 362 | 718 | 27.6 | 0 |
| 5. Xylene | 1,137 | 71.0 | 458 | 7.74 | 0 |
| 6. Styrene | 1,189 | 2,701 | 4,131 | 196 | 24.8 |
| Total hydrocarbon ^b | 132,632 | 57,931 | 5,684 | 327 | 64 |
| Volume (%) | | | | | |
| Measured hydrocarbon as compound | 13.3 | 5.76 | 0.57 | 0.03 | 0.01 |
| O ₂ | 5.27 | 10.65 | 19.10 | 19.56 | 19.65 |
| N ₂ | 76.99 | 77.71 | 74.21 | 77.01 | 76.53 |
| CO ₂ | 1.55 | 0.64 | 0.15 | 0.006 | ND |
| H ₂ O | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 98.62 | 96.27 | 95.53 | 101.71 | 97.70 |
| Hydrocarbon emission/production rate (lb/gal) | 0.037 | 0.043 | 0.00050 | 0.000082 | ID |

^a Average of 11 runs from two days. Results should be reviewed from individual analyses and not from an average (see sub-summaries).

^b reviewed from individual analyses and not from an average (see sub-summaries).

^c Average of 3 runs from one day.

^d Represents one run.

^e Concentration values are on a dry basis.

^f No emission point to atmosphere.

^j Average of two runs.

^g Condensate values not included see sub-summary tables.

^h Pounds of hydrocarbon emissions per gallon of latex processed.

ⁱ Average rate of two days tested.

NA - No measurements parameters available.

ID - Insufficient data to calculate rate

consistent so that the averages are representative of the emissions associated with the operating process. The emissions from the steam stripper and storage tank are considerably less than the emissions from the central vacuum system. The end result of the processes tested was a total average emission rate of 57.5 lb/hr hydrocarbons found under normal operating conditions. This total figure does not include the blowdown outlet emission rate because this gas stream was routed to the central vacuum system for emission into the atmosphere.

2.2.2 Blowdown Tank Outlet

The hydrocarbon emissions from the blowdown tank were not vented directly to the atmosphere (Table 2-1). However, a study of the emissions is important in a study of possible control devices. The emissions from the blowdown tank are averaged in Table 2-1. This is the average of tests from 2 days of sampling, and does not accurately reflect the emission rate. During the period of a reactor dump the emissions were high and decreased significantly over the next several hours of the degassing period. The emission profile is discussed at length in Section 3. The results from this location are much clearer if each sample is discussed separately.

2.2.3 Styrene Mass Balance

The third analytical problem was to study a mass balance of styrene around the blowdown tank and the steam stripper. The mass balance was determined by calculating the total styrene entering the tank and leaving the tank. Styrene entered the tanks in the latex which had a known flow rate. A sample of the entering latex was analyzed for the residual styrene content by gas chromatography (Section 6.2). The styrene left the tanks either in the latex or as a gas. Samples of gas outlets and latex outlets were analyzed by gas chromatography for the styrene content. Flow rates were monitored for both the gas samples and latex samples. The results show mass balances for both tests of the blowdown tank and all three tests of the steam stripper. The tables in Section 3.2 represent the mass balance results of the two systems.

2.3 HYDROCARBON EMISSION RATE PER GALLON OF SBR LATEX PROCESSED

The production rate of SBR latex was calculated. The hydrocarbon emission rate were determined by testing. The calculations of the

emission/production rate was determined for the blowdown tank system, the central vacuum system outlet, the styrene stripper outlet, and the storage tank outlet. The hydrocarbon emission rate utilized the results of the tests at the sample locations in the process. The production rate of SBR latex was supplied by plant personnel.

The production rate of the blowdown tank outlet and central vacuum system was determined from the amount of latex produced in the three reactors dumping into blowdown tank #4 (BDT #4). The time period of testing this process was from the initial reactor dumping into BDT #4 until the latex was transferred from BDT #4 to the shaker screen system. The emission rate of hydrocarbon was averaged because the source of the emission was a batch operation. The emission/production rate of the 2 days of monitoring the process through BDT #4 was 0.037 pounds of hydrocarbon per gallon of latex produced (lb/gal) for the blowdown tank outlet (see sample calculation in Appendix A); and 0.043 lb/gal for the central vacuum system outlet.

The emission/production rates of the steam stripper outlet and storage tank outlet were determined by the emissions from the continuous process through the stripper system that filled the storage tank tested. The emissions were determined over an 8-hour period during the operation of the stripper. The production rate used was the average gallons of latex feeding into the stripper system during the test period. The results of the emission/production rate calculation was 5.10×10^{-4} lb/gal at the steam stripper outlet and 8.2×10^{-5} lb/gal at the storage tank outlet.

3.0 DISCUSSION OF RESULTS

The primary objectives of the test at the Mogadore facility were to determine the total volatile organic emissions (Section 3.1), to observe a mass balance of styrene around the steam stripper (Section 3.2), a mass balance of styrene around the blowdown tank (Section 3.3), to characterize the butadiene emission peak associated with a reactor dump for the purpose of design criteria for control devices (Section 3.4), and rates of organic compounds in the gaseous and latex samples (Section 3.5).

3.1 TOTAL VOC EMISSIONS

Gaseous samples were collected at the following emission points: the central vacuum system outlet (Section 3.1.1), the fugitive emission of the shaker screens (Section 3.1.2), the steam stripper vacuum system outlet, (Section 3.1.3), and the product storage tank (Section 3.1.4). The process, pertaining to the emission locations will be discussed, briefly for each location. A note of caution should be made against using the average results to represent the VOC emissions (Table 2-1); the individual analytical results show that the emissions reflect the cyclic process pattern around the blowdown tank process. A modified sample location (#1A) was maintained at the blowdown tank outlet (Section 3.1.5) to obtain concentration results of the gas stream before the condenser in line to the emission point at the central vacuum system exhaust.

3.1.1 Central Vacuum System Outlet (Sample Location #1)

In the plant process the raw styrene and butadiene were combined in reactors to produce the SBR latex. Normally, three batches would dump into one blowdown tank. There were four blowdown tanks in the Mogadore facility. The emissions from all the blowdown tanks were channeled

through a condenser and then vented to the atmosphere through the central vacuum system. Gas samples were collected at the outlet of the central vacuum system during two sets of the reactor dumps and degassing cycles. Samples were collected following the modified EPA Method 110 (Appendix G). Temperature and flow measurements were taken throughout the course of the test (Section 6). The first reactor dump degassing cycle lasted approximately 8½ hours. During that time the emission temperatures rose and then decreased. The flow rate also increased and then decreased (Table 3-1). Over the course of the test the total hydrocarbon emission rate showed dramatic changes: 47.8 lb/hr for the first hour, 89.7 lb/hr and 90.6 lb/hr average over the next 5 hours. For individual hydrocarbons, the results show a gradual decrease in concentration except for styrene, which shows a marked increase in concentration over time (Table 3-1). The hydrocarbon measurements were performed by GC/FID analysis (Section 6.2) the stationary gas analyses were performed by GC/TCD (Section 6.2).

The second monitored reactor dump and degassing cycle lasted approximately 8 hours. During the first day of testing, liquid condensate was observed in the sample line, therefore the integrated bag sampling method was modified by placing a condensate trap in the sampling line to remove the liquid condensate that came through the sampling line. The collected condensate was analyzed by the direct injection technique into the GC/FID (Section 6.2). The condensate had a water phase and an organic phase. The organic phase contained 31.91 percent total hydrocarbons by volume with the remainder being an inorganic solution, and the water phase contained 0.15 percent total hydrocarbons by volume (Table 3-2). The condensate hydrocarbon values were added to the average gaseous hydrocarbon values to give the total hydrocarbon emission rate reported for the test.

Temperature and flow measurements were taken throughout the course of the test (Section 6.4). During the test the temperature rose steadily. The flow rate increased in the first hour and decreased after that (Table 3-2). The comparison of the flow rates for the first test and the second test shows that the flows on the second day were considerably lower.

Table 3-1. TEST RESULTS FROM THE CENTRAL VACUUM
SYSTEM OUTLET (SAMPLE POINT 1)

| Date | 3/27/80 | 3/27/80 | 3/27/80 | 3/27/80 | Average ^c |
|--|--------------------|-----------|-----------|-----------|----------------------|
| Time | 0906-1002 | 1002-1102 | 1102-1236 | 1236-1731 | |
| Run number | 1 | 1 | 1 | 1 | |
| Integrated bag number | A | B | C | D | |
| Process Data | | | | | |
| Flue gas temperature (°F) | 85 | 123 | 155 | 107 | 115 |
| Flue gas area (ft ²) | 0.087 | 0.087 | 0.087 | 0.087 | 0.087 |
| Flow rate (SCFM) | 134.41 | 163 | 131 | 101.30 | 117.83 |
| Emission rate (lb/hr) | 47.8 | 89.7 | 90.6 | 82.2 | 80.8 |
| Analytical Results ^a (ppmv as compound) | | | | | |
| 1. Butadiene | 75,424 | 62,512 | 69,670 | 70,062 | 69,687 |
| 2. Benzene | 8.6 | 3.6 | 1.0 | 13.2 | 9.3 |
| 3. Toluene | 16.7 | 15.6 | 1.3 | 11.1 | 10.4 |
| 4. Ethylbenzene | 601 | 577 | 309 | 323 | 381 |
| 5. Xylene | 122 | 168 | 113 | 104 | 115 |
| 6. Styrene | 1,928 | 2,147 | 2,767 | 4,338 | 3,518 |
| Total hydrocarbon | 78,100 | 65,423 | 72,862 | 74,851 | 73,721 |
| Volume (%) | | | | | |
| Measured hydrocarbon as compound | 7.8 | 6.5 | 7.3 | 7.5 | 7.4 |
| O ₂ | 6.48 | 5.17 | 7.48 | 8.38 | 7.62 |
| N ₂ | 58.14 | 80.48 | 72.80 | 76.10 | 74.01 |
| CO ₂ | 0.73 | 0.43 | 1.41 | 0.68 | 0.79 |
| H ₂ O | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 74.66 ^b | 94.09 | 90.50 | 94.17 | 91.31 |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to those retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

^bThe total % of gases analyzed only total 74.66%. Since 25% is unaccounted for, these numbers should be considered suspect.

^cThe average is a "time weighted average" of the concentration value and lb per hour values.

Table 3-2. TEST RESULTS FROM THE CENTRAL
VACUUM SYSTEM (SAMPLE POINT 1)

| Date | 4/1/80 | 4/1/80 | 4/1/80 | 4/1/80 | Average ^c |
|---|-------------------|-----------|-----------|-----------|----------------------|
| Time | 0728-0855 | 0900-1035 | 1040-1355 | 1405-1535 | |
| Run Number | 2 | 2 | 2 | 2 | |
| Integrated Bag Number | A | B | C | D | |
| Process Data | | | | | |
| Flue Gas Temp. (°F) | 84 | 98 | 118 | 121 | 108 |
| Flue Gas Area (Ft ²) | 0.087 | 0.087 | 0.087 | 0.087 | 0.087 |
| Flow Rate (SCFM) | 98.31 | 130.52 | 72.78 | 89.19 | 92.44 |
| Emission Rate (Lb/Hr) | 62.3 | 88.7 | 16.0 | 5.3 | 37.4 |
| Analytical Results^a (ppmv as compound) | | | | | |
| 1. Butadiene | 72552 | 77919 | 21562 | 3494 | 39329 |
| 2. Benzene | 28.4 | 11.7 | 35.2 | 36.5 | 37.6 |
| 3. Toluene | 23.0 | 10.7 | 17.8 | 15.3 | 20.3 |
| 4. Ethylbenzene | 398 | 366 | 223 | 245 | 344 |
| 5. Xylene | 21.2 | 27.6 | 23 | 18.9 | 27.1 |
| 6. Styrene | 1599 | 1734 | 2058 | 1610 | 1884 |
| Total Hydrocarbon ^b | 74622 | 80069 | 23919 | 5419 | 42142 |
| Volume % | | | | | |
| Measured Hydrocarbon as Compound | 7.5 | 8.0 | 2.39 | .54 | 4.13 |
| O ₂ | 13.0 | 11.6 | 15.51 | 12.55 | 13.68 |
| N ₂ | 77.81 | 79.75 | 83.93 | 81.15 | 81.40 |
| CO ₂ | 1.2 | .38 | .37 | .19 | 0.49 |
| H ₂ O | 1.51 ^d | 1.51 | 1.51 | 1.51 | 1.51 |
| Total % | 101.01 | 101.21 | 103.71 | 95.91 | 101.21 |
| Unaccounted for % | -- | -- | -- | 4.09 | -- |

^aNot representative if interested in control device fabrication - concentration varies widely from average.

^bDoes not include condensate results - At this location 480 ml condensate collected in 0810 hrs.; condensate contains 32.06% hydrocarbons by volume.

^cTime weighted average over test period.

^dBased on saturation at analyses temperature.

The total emission rate for the second test period reflect the process pattern. When the reactor dump began, the emission rates of the first 2 hours were 62.3 lb/hr and 88.7 lb/hr. Only one sample was collected over the next 4 hours, and the emission rate was 16.0 lb/hr. The last hours of the degassing period showed 5.3 lb/hr (Table 3-2). This increasing and then decreasing emission rate was seen both days that the central vacuum system was tested. On the second day of testing both the flow rate and measured hydrocarbon concentrations were lower than the first day. A possible reason for this change was a process interruption in the central vacuum system. A noticeable decrease in hydrocarbon concentration coincides with the system shut-down.

During the second week of testing (4/1/80), the CVS developed an operational problem for several hours. A valve on the knockout pot prior to the pumps malfunctioned, allowing entrained liquid from the knockout pot past the vacuum pumps and into the exhaust line. During this period (0920 hrs - 0945 hrs), the additional pressure from the liquid may have caused inaccurate pressure readings at the D_p cell and magnehelic. The system malfunction was evidenced by a white latex-like rain exiting from the system atmospheric exhaust. Corrective action by plant maintenance personnel solved the problem quickly and no further system disruptions were encountered. A second significant process difference between the 2 days was the condensate associated with the gas emissions on the second day.

The emissions associated with blowdown tanks and the central vacuum system vary widely from the averages. In the summary table (Table 2-1) the central vacuum system emission results are the average of the results from both days of testing. The results from the second day include the results of the condensate analyses. A note should be made that the real emissions follow a pattern of high levels during the reactor blowdown with decreasing levels as the degassing process continues. The average would not reflect this pattern.

3.1.2 Fugitive Emissions of the Shaker Screens (Sample Location #3)

The second emission point in the process was above the shaker screens. The latex flowed from the blowdown tanks through a series of

screens which separated out any congealed latex. The screens were open to the atmosphere so no flow measurements were obtained. The concentration of hydrocarbons being emitted from the screens were very low, (Table 3-3) amounting to 64 ppm by volume total. Only one sample was collected from the surface above the screens. The sample was collected following the modified EPA Method 110 (Appendix G), and was analyzed by GC/FID (Appendix F).

3.1.3 Steam Stripper Vacuum System Exhaust (Sample Location #2)

As the latex proceeded, the next stage was the pre-blend tank. From there the latex flowed to one of two steam strippers. Steam was forced through the latex to remove any residual hydrocarbons, primarily styrene. The emissions from both steam strippers were vented through the steam stripper vacuum system. Three gas samples were collected at the steam stripper vacuum system outlet following the modified EPA Method 110 (Appendix G). Flow rates and temperatures were monitored during the sampling period (Section 6.4). The temperatures and the flow rates remained consistent throughout the test. The total hydrocarbon concentrations in each samples were found to be close to the average 5600 ppm by volume (Table 3-4). The flow rate was quite low and the average hydrocarbon emission rate was 1.2 lb/hr. The averages appear representative of the conditions and emissions during operation of the steam stripper vacuum system.

3.1.4 Product Storage Tank Outlet (Sample Location #11)

The final emission point analyzed was the outlet above the product storage tank. Three gas samples were collected at the outlet following the modified EPA Method 110 (Appendix G). Flow and temperature measurements were made throughout the sampling period (Section 6.4). The temperature and flow rates were consistent in each test. The average flow rate was low, 6.38 SCFM average (Table 3-5). The total hydrocarbon concentration in each sample was approximately 330 ppm (by volume). Therefore, the average hydrocarbon emission rate was 0.20 lb/hr (Table 3-5). The averages appear to be representative of the conditions associated with the product storage tank.

3.2 MASS BALANCE OF STYRENE AROUND THE BLOWDOWN TANK

The mass balance around the blowdown tank was based on a comparison of residual styrene found in the latex at the blowdown tank outlet plus

Table 3-3. TEST RESULTS FROM THE FUGITIVE
EMISSIONS OF THE SHAKER SCREENS
(SAMPLE POINT 3)

| | |
|--|-----------|
| Date | 4/2/80 |
| Time | 1730-1800 |
| Run number | 1 |
| Integrated bag number | A |
| Process Data | |
| Flue gas temperature (°F) | 103 |
| Flue gas area (ft ²) | NA |
| Flow rate (SCFM) | NA |
| Emission rate (lb/hr) | NA |
| Analytical Results ^a (ppmv as compound) | |
| 1. Butadiene | 39.2 |
| 2. Benzene | 0 |
| 3. Toluene | 0 |
| 4. Ethylbenzene | 0 |
| 5. Xylene | 0 |
| 6. Styrene | 24.8 |
| Total hydrocarbon as compound | 64 |
| Volume (%) | |
| Measured hydrocarbon as compound | 0.006 |
| O ₂ | 19.65 |
| N ₂ | 76.53 |
| CO ₂ | ND |
| H ₂ O | 1.51 |
| Total (%) | 97.71 |
| Unaccounted for (%) | 2.29 |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to those retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

Table 3-4. TEST RESULTS FROM THE STEAM STRIPPER
EXHAUST (SAMPLE POINT 2)

| Date | 4/2/80 | 4/2/80 | 4/2/80 | Average ^b |
|--|-----------|-----------|-----------|----------------------|
| Time | 1217-1250 | 1250-1510 | 1510-1638 | |
| Run number | 1 | 1 | 1 | |
| Integrated bag number | A | B | C | |
| Process Data | | | | |
| Flue gas temperature (°F) | 65 | 60 | 57 | 60 |
| Flue gas area (ft ²) | 0.09 | 0.09 | 0.09 | 0.09 |
| Flow rate (SCFM) | 8.02 | 8.23 | 6.16 | 7.51 |
| Emission rate (lb/hr) | 0.6 | 1.5 | 0.9 | 1.2 |
| Analytical Results ^a (ppmv as compound) | | | | |
| 1. Butadiene | 318 | 368 | 366 | 366 |
| 2. Benzene | 8.6 | 3.4 | 0 | 2.9 |
| 3. Toluene | 12 | 14.4 | 10.9 | 12.9 |
| 4. Ethylbenzene | 574 | 801.5 | 638.5 | 718 |
| 5. Xylene | 363 | 494 | 437 | 458 |
| 6. Styrene | 3,392 | 4,884 | 3,209 | 4,131 |
| Total hydrocarbon as compound | 4,668 | 6,566 | 4,662 | 5,684 |
| Volume (%) | | | | |
| Measured hydrocarbon as compound | 0.47 | 0.66 | 0.47 | 0.57 |
| O ₂ | 19.26 | 18.76 | 19.50 | 19.10 |
| N ₂ | 76.41 | 71.46 | 77.80 | 74.21 |
| CO ₂ | 0.15 | ND | ND | 0.15 |
| H ₂ O | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 97.81 | 92.41 | 99.31 | 95.53 |
| Unaccounted for (%) | 2.19 | 7.59 | 0.69 | 4.47 |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to those retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

^bThe average is a "time weighted average" of the concentration values and lb per hour values.

Table 3-5. TEST RESULTS FROM THE STORAGE
TANK VENT (SAMPLE POINT 11)

| Date | 4/2/80 | 4/2/80 | 4/2/80 | Average ^b |
|--|-----------|-----------|-----------|----------------------|
| Time | 1147-1202 | 1245-1345 | 1540-1640 | |
| Run number | 1 | 1 | 1 | |
| Integrated bag number | A | B | C | |
| Process Data | | | | |
| Flue gas temperature (°F) | 55 | 96 | 95 | 91 |
| Flue gas area (ft ²) | 0.087 | 0.087 | 0.087 | 0.087 |
| Flue rate (SCFM) | 6.84 | 6.33 | 6.32 | 6.38 |
| Emission rate (lb/hr) | 0.2 | 0.2 | 0.2 | 0.2 |
| Analytical Results^a (ppmv as compound) | | | | |
| 1. Butadiene | 63.8 | 56.7 | 52.9 | 55.8 |
| 2. Benzene | 0 | 0 | 0 | 0 |
| 3. Toluene | 38.4 | 40.4 | 39.9 | 40.0 |
| 4. Ethylbenzene | 26.1 | 24.5 | 31.1 | 27.6 |
| 5. Xylene | 8.9 | 13.1 | 2.1 | 7.7 |
| 6. Styrene | 210 | 195 | 196 | 196 |
| Total hydrocarbon as compound | 348 | 328 | 322 | 327 |
| Volume (%) | | | | |
| Measured hydrocarbon as compound | 0.03 | 0.03 | 0.03 | 0.03 |
| O ₂ | 19.29 | 19.08 | 20.10 | 19.56 |
| N ₂ | 76.33 | 74.19 | 80.07 | 77.01 |
| CO ₂ | 0.06 | 0.06 | ND | 0.06 |
| H ₂ O | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 97.21 | 94.91 | 101.71 | 98.17 |
| Unaccounted for (%) | 2.79 | 5.09 | -- | 1.83 |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to the retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

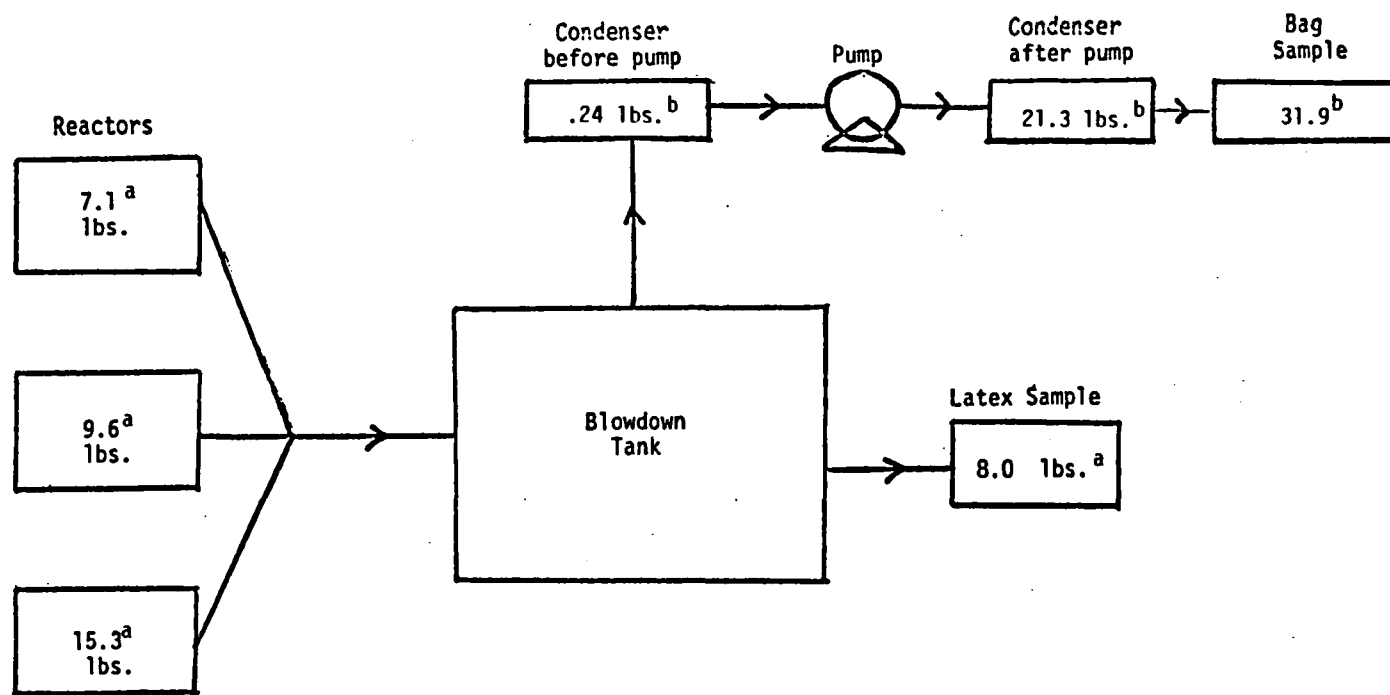
^bThe average is a "time weighted average" of the concentration values and lb per hour values.

the gaseous emissions of styrene found at the outlet of the blowdown tank to the residual styrene found in the latex at the inlet of the blowdown tank (Figure 3-1). Three reactors flowed latex into the blowdown tank. The gallons of residual styrene in each reactor were calculated from the total volume of latex and the percent of residual styrene per gallon of latex (Appendix B). The percent of residual styrene was determined by direct injection of the latex sample into a GC/FID as prescribed in the EPA Draft method for the Determination of Residual Styrene (Appendix F). A sample of latex from each reactor was analyzed (Appendix B). The total pounds of residual styrene entering the blowdown tank was 32.09 (Table B-5).

The styrene left the blowdown tank either as a gas or by remaining in the latex. The residual styrene content in the latex leaving the blowdown tank was determined by GC/FID analysis of a prepared latex sample as described in the EPA Draft method for the Determination of Residual Styrene. The total pounds of styrene leaving the blowdown tank in the latex were the results of the GC/FID analyses (Appendix C) multiplied by the (7.7 pounds/gallon density) and the total pounds of latex leaving the blowdown tank (Appendix B).

The styrene content leaving the blowdown tank as a gas was difficult to measure. Condensation of the gas occurred around the pump so that condensate traps were placed before and after the pump. The condensate samples were analyzed by direct injection into a GC/FID in the same manner as a latex sample. The analytical results multiplied by the volume of condensate gave the production of styrene per sampled volume of gas; therefore, the weight per sample was multiplied by the ratio of the total gas volume with the sampled gas volume to give a result of pounds of styrene per sample period (Appendix B).

The concentration of styrene collected in the bag samples was determined by GC/FID analysis (Section 6.2). Conversion of ppm styrene, by volume, to total pounds of styrene appears in Appendix B. The pounds of styrene leaving the blowdown tank as a gas was considered to be the sum of the styrene in the bag samples plus the styrene in the condensate samples (Figure 3-1). The total styrene, then, leaving the blowdown tank as either gas or latex was 61.5 lbs (Figure 3-1).



^aOn a dry basis.

^bOn a wet basis - no dry basis was possible due to only volatile hydrocarbons being present.

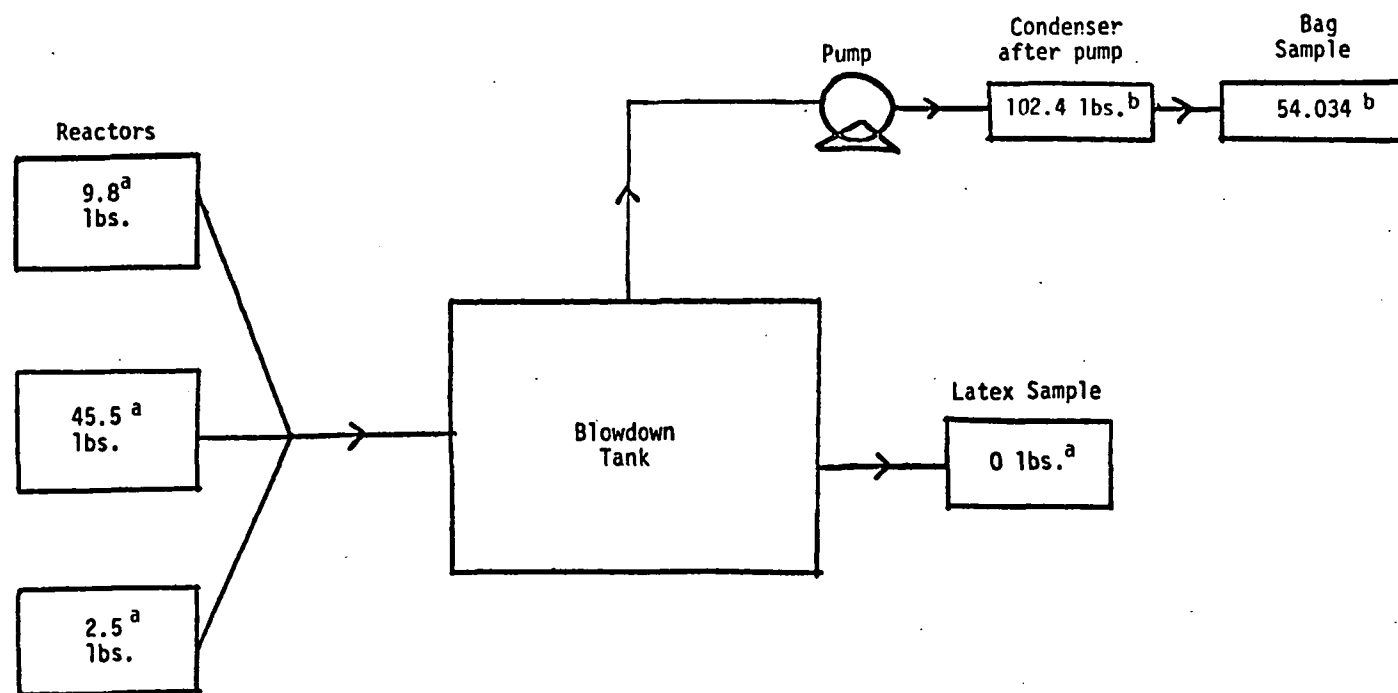
Figure 3-1. Mass balance of styrene around the blowdown system on 3/27/80.

A second mass balance determination was performed around the blowdown system (Figure 3-2). Analysis of the latex samples from the three reactors showed 57.8 lbs of styrene going into the blowdown tank (Appendix B, Table B-6). The pounds of styrene leaving the blowdown tank was 156.4 lbs. The latex samples were analyzed by draft procedures that presents the results on a dry basis. An attempt to calculate the gas and condensate from the wet basis to a dry basis is not applicable due to the analysis method and sample composition. One unusual result was that no residual styrene was found in the latex sample collected at the outlet of the blowdown tank. We can suggest no possible explanation even after double checking all analytical systems. All the latex samples and the condensate samples were analyzed by GC/FID following the EPA Draft method for the Determination of Residual Styrene (Appendix F). The gas samples were also analyzed by GC/FID (Section 6.2).

Analysis of the gaseous samples and condensate samples for their styrene content by GC/FID permitted identification of all the hydrocarbon species present in the samples (Tables 3-6 and 3-7). The results shown for the blowdown tank (Tables 3-6 and 3-7) indicate the concentrations of hydrocarbons that would be vented to the atmosphere if the condenser was not in-line prior to the central vacuum system (Section 3.1). Some rough estimations of emissions after the condenser may be made by assuming that the condensate traps used for sampling simulated the plant's condenser system, and then looking at only the gaseous portion of the sample. However, no attempt was made to duplicate condenser operating conditions. On the first day of sampling the average gaseous hydrocarbon concentration was 4.4 percent by volume. The condensate associated with the gas stream was collected during the 8-hour sampling period. A total of 454 ml was collected (Table A-9) which contained 22.73 percent hydrocarbons by volume. On the second day of testing the average total gaseous hydrocarbon concentration was 20.69 percent by volume. A total of 3553 ml of condensate was collected over the 8-hour sampling period (Appendix B) and contained 1.72 percent hydrocarbons by volume.

3.3 MASS BALANCE OF STYRENE AROUND THE STEAM STRIPPER

Latex samples were collected at the inlet and the outlet of the steam stripper. The mass balance of styrene was determined by comparing



^aOn a dry basis.

^bOn a wet basis - no dry basis was possible due to only volatile hydrocarbons being present.

Figure 3-2. Mass Balance of styrene around the blowdown system on 4/1/80.

Table 3-6. TEST RESULTS FROM THE BLOWDOWN TANK OUTLET
(SAMPLE POINT 1A)

| Date | 3/27/80 | 3/27/80 | 3/27/80 | 3/27/80 | 3/27/80 | 3/27/80 | Average ^c |
|--|----------|-----------|-----------|-----------|-----------|-----------|----------------------|
| Time | 905-1004 | 1007-1225 | 1230-1425 | 1438-1620 | 1630-1650 | 1705-1740 | |
| Run number | 1 | 1 | 1 | 1 | 1 | 1 | |
| Integrated bag number | A | B | C | D | E | F | |
| Process Data | | | | | | | |
| Flue gas temperature (°F) | e | | | | | | |
| Flue gas area (ft ²) | f | | | | | | |
| Flow rate (SCFM) | 65 | 59.44 | 15.10 | 57.35 | 116.72 | 142.17 | 57.42 |
| Emission rate (lb/hr) ^d | 23.4 | 14.1 | 5.0 | 30.4 | 112.0 | 47.8 | 31.6 ^g |
| Analytical Results^a (ppmv as compound) | | | | | | | |
| 1. Butadiene | 41,580 | 25,799 | 37,154 | 59,026 | 104,372 | 25,505 | 41,198 |
| 2. Benzene | 2.2 | 0.2 | 0 | 7.1 | 71 | 153 | 16.3 |
| 3. Toluene | 219 | 207 | 215 | 392 | 1,291 | 1,648 | 404 |
| 4. Ethylbenzene | 138 | 161 | 186 | 358 | 998 | 1,394 | 335 |
| 5. Xylene | 73 | 103 | 109 | 195 | 543 | 1,403 | 237 |
| 6. Styrene | 617 | 1,011 | 1,125 | 1,713 | 3,227 | 3,372 | 1,413 |
| Total hydrocarbon as compound ^b | 42,630.4 | 27,281 | 38,789 | 61,691 | 110,501 | 34,475 | 43,603 |
| Volume (%) | | | | | | | |
| Measured hydrocarbon as compound | 4.3 | 2.7 | 3.9 | 6.2 | 11.0 | 3.4 | 4.4 |
| O ₂ | 5.41 | 4.81 | 5.65 | 8.44 | 9.98 | 13.43 | 6.74 |
| N ₂ | 78.84 | 78.84 | 77.53 | 58.58 | 70.63 | 82.68 | 74.04 |
| CO ₂ | 2.01 | 1.23 | 0.75 | 2.61 | 1.33 | 0.34 | 1.45 |
| H ₂ O @ 55° | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 92.07 | 89.09 | 89.34 | 77.34 | 94.45 | 101.36 | 88.14 |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to the retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

^bAs noted below, varying percentages (from 77 to 101 percent) of the total volume of gases present were accounted for in the analysis procedures for O₂, N₂, CO₂, and hydrocarbons. Therefore, the reader should be careful in interpreting these results.

^cThe average is a "time weighted average" of the concentration values and lb per hour values.

^dNo emission vent to atmosphere, therefore, results is the gas stream concentration rate to the condenser in line to the central vacuum system.

^eNo data - dial thermometer in gas stream installed for 4/1/80 test day at sample point 1A.

^fNo vent to atmosphere but flow determined with an orifice installed with a differential pressure gauge.

^gThe total hydrocarbon emission rate of 31.6 was calculated with the addition of the 8.27 lb/hr in the sampled condensate (see Table A-9). The time weighted average of hydrocarbon emission rate without the condensate was 23.3 lb/hr.

Table 3-7. TEST RESULTS FROM THE BLOWDOWN TANK OUTLET
(SAMPLE POINT 1A)

| Date | 4/1/80 | 4/1/80 | 4/1/80 | 4/1/80 | 4/1/80 | Average ^c |
|--|-----------|-----------|-----------|-----------|-----------|----------------------|
| Time | 0726-1824 | 0827-0944 | 0945-1159 | 1204-1420 | 1437-1603 | |
| Run number | 2 | 2 | 2 | 2 | 2 | |
| Integrated bag number | A | B | C | D | E | |
| Process Data | | | | | | |
| Flue gas temperature (°F) | 140 | 135 | 145 | 161 | 165 | 151 |
| Flue gas area (ft ²) | e | | | | | |
| Flow rate (SCFM) | 175.75 | 181.79 | 87.46 | 196.47 | 221.64 | 166.54 |
| Emission rate (lb/hr) ^d | 32.8 | 177.7 | 31.4 | 23.8 | 55.7 | 68.5 ^f |
| Analytical Results^a (ppmv as compound) | | | | | | |
| 1. Butadiene | 143,148 | 275,239 | 216,994 | 312,355 | 61,388 | 216,563 |
| 2. Benzene | 68.2 | 72.5 | 119 | 138 | 95.2 | 107 |
| 3. Toluene | 132.5 | 91.1 | 47.5 | 40.1 | 22.0 | 57.9 |
| 4. Ethylbenzene | 162 | 399 | 429 | 736 | 726 | 530 |
| 5. Xylene | 56.1 | 180 | 213 | 435 | 10,391 | 2,037 |
| 6. Styrene | 912 | 1,907 | 2,249 | 2,996 | 2,945 | 2,366 |
| Total hydrocarbon as compound ^b | 144,479 | 277,889 | 220,051 | 316,700 | 78,845 | 221,661 |
| Volume (%) | | | | | | |
| Measured hydrocarbon as compound | 14.4 | 27.8 | 22.0 | 31.7 | 7.9 | 22.2 |
| O ₂ | 2.38 | 5.14 | 3.76 | 3.76 | 3.76 | 3.81 |
| N ₂ | 75.96 | 83.65 | 79.80 | 79.80 | 79.80 | 79.95 |
| CO ₂ | 2.38 | 1.0 | 1.69 | 1.69 | 1.69 | 1.66 |
| H ₂ O | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 | 1.51 |
| Total (%) | 96.63 | 119.11 | 108.76 | 118.46 | 94.66 | 109.13 |
| Unaccounted for (%) | 3.37 | -- | -- | -- | 5.34 | -- |

^aThese data represent those compounds expected to be present and identified as that compound by virtue of having similar retention times to the retention times of these known gases. The retention times of the known (reference) gases were determined by laboratory injection under similar GC operations.

^bAs noted below, varying percentages for O₂, N₂, CO₂ and hydrocarbons. Therefore, the reader should be careful in interpreting these results.

^cThe average is a "time weighted average" of the concentration values and lb per hour values.

^dNo emission vent to atmosphere, therefore, results are the gas stream concentration rate to the condenser in line to the central vacuum system.

^eNo vent to atmosphere but flow determined with an orifice installed with a differential pressure gauge.

^fThe total hydrocarbon emission rate of 78.8 was calculated with the addition of the 10.3 lb/hr in the sampled condensate (see Table A-9). The time weighted average of hydrocarbon emission rate without the condensate was 68.5 lb/hr.

the pounds of residual styrene entering the steam stripper in the latex to the styrene leaving the steam stripper in the gaseous emissions and in the latex. Three separate mass balances were determined (Figure 3-3). The residual styrene in the latex samples was determined by GC/FID analysis (Appendix F). The total amount of styrene entering and leaving the stripper in latex was calculated from the analytical results (Appendix C) and the total volume transferred. The styrene escaping the stripper as a gas was collected as an integrated bag sample (modified EPA Method 110) and analyzed by GC/FID. In all three test periods correlation between styrene into and out of the system was found (Figure 3-3). In the first test 1.95 lbs was calculated going in, and 1.16 lbs was calculated going out (Appendix B). In the second test, 1.82 lbs was calculated going into the stripper with 1.80 lbs coming out (Appendix B). In the third test, 0.72 lbs styrene was calculated going into the stripper with 0.51 lbs coming out (Appendix B).

3.4 PEAK CHARACTERIZATION OF BUTADIENE AND STYRENE EMISSIONS

During the transfer of latex from the reactor to the blowdown tank the butadiene emissions increased and decreased significantly while the styrene emissions over the same period increased steadily. The transfer period lasted approximately 30 minutes. These peak emissions are significant for the development of possible control systems. To characterize the emissions over one of these transfer periods, integrated grab bag samples were collected every 5 minutes following the modified EPA Method 110 (Appendix D). Analysis of the gas samples was performed by GC/FID (Section 6.2). The results (Table A-12) indicate that the butadiene concentration rose from 143,000 ppm by volume to 312,000 ppm by volume in the first 20 minutes. In the following 5 minutes the butadiene concentration dropped to 61,000 ppm by volume (Figure 3-4). The styrene concentrations, over the same 25-minute period, rose from 1,200 ppm by volume to 3,200 ppm by volume (Figure 3-5).

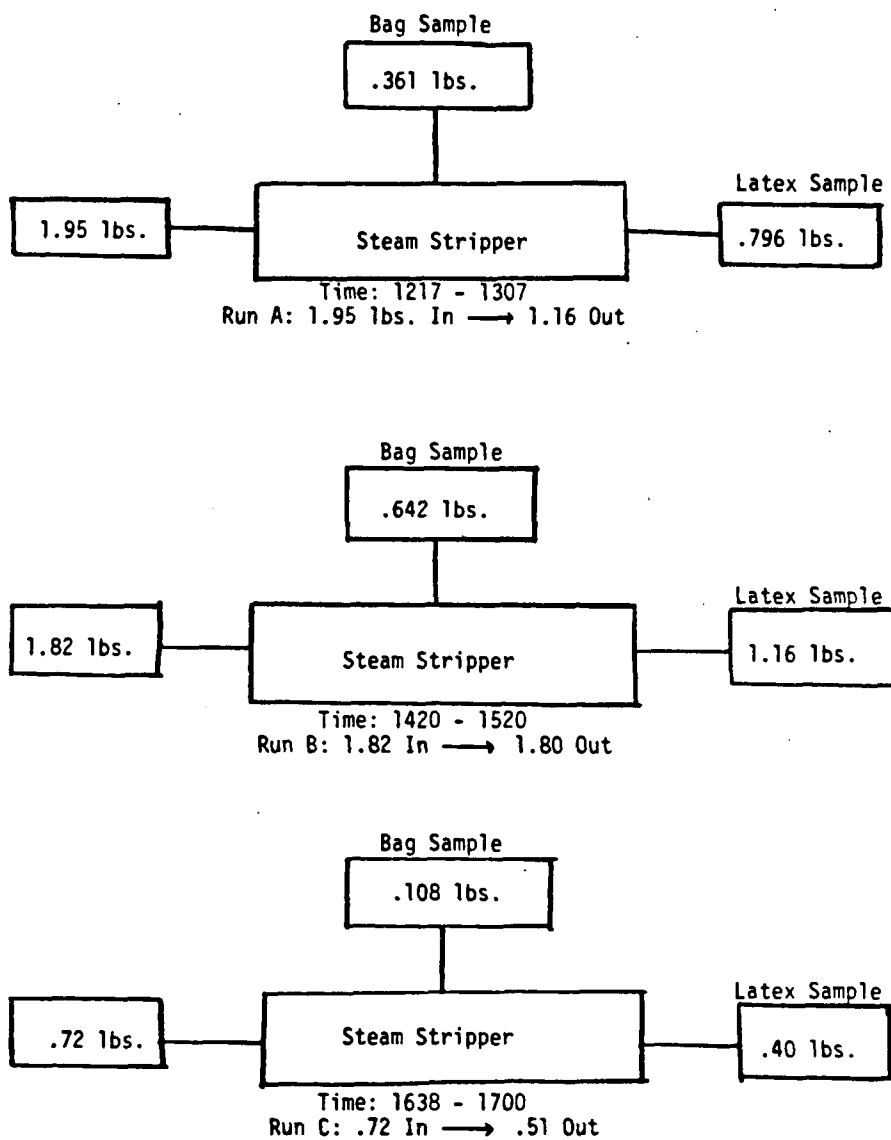


Figure 3-3. Mass Balance of Styrene Around the Steam Stripper on 4/1/80

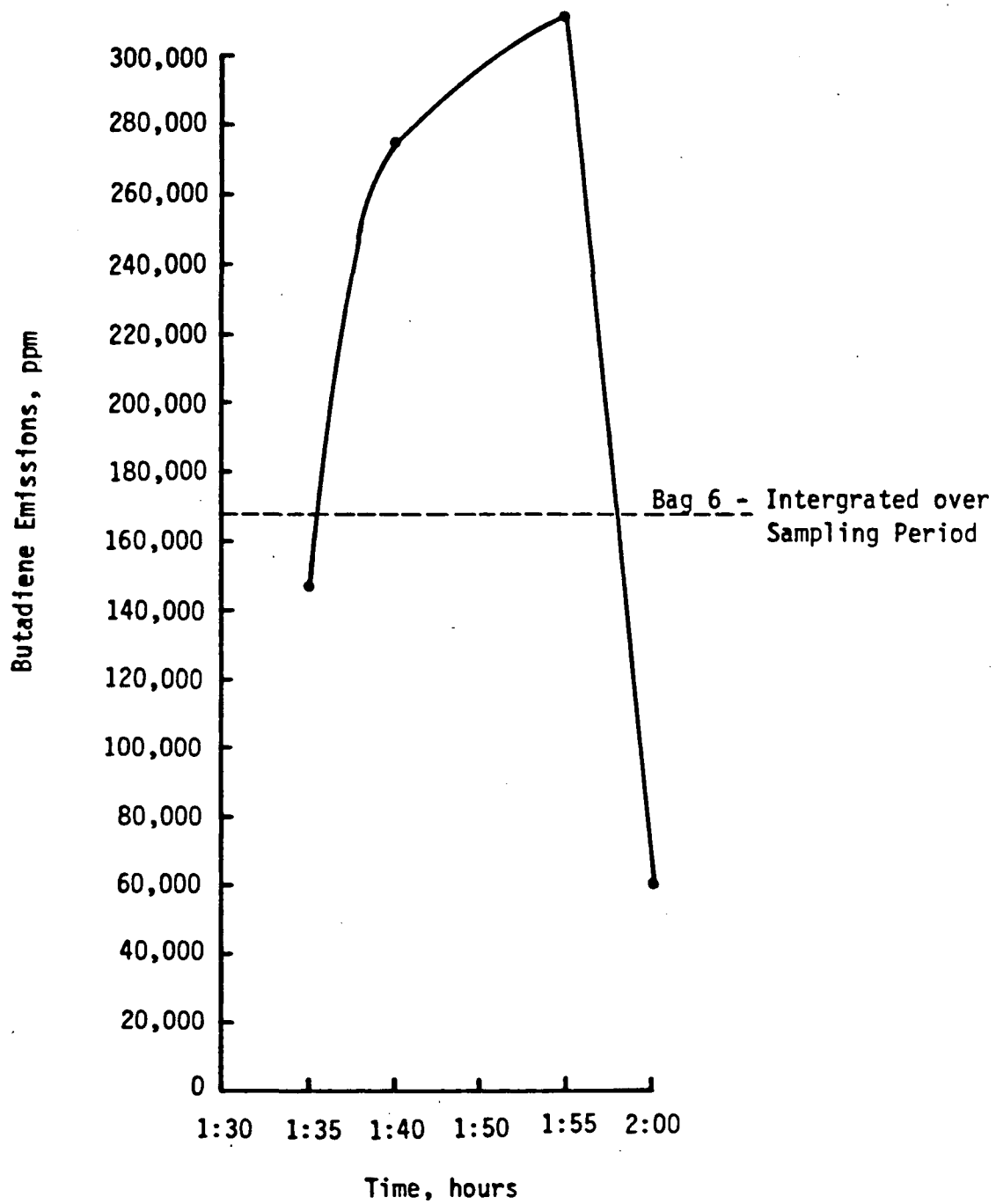


Figure 3-4. Butadiene Emissions

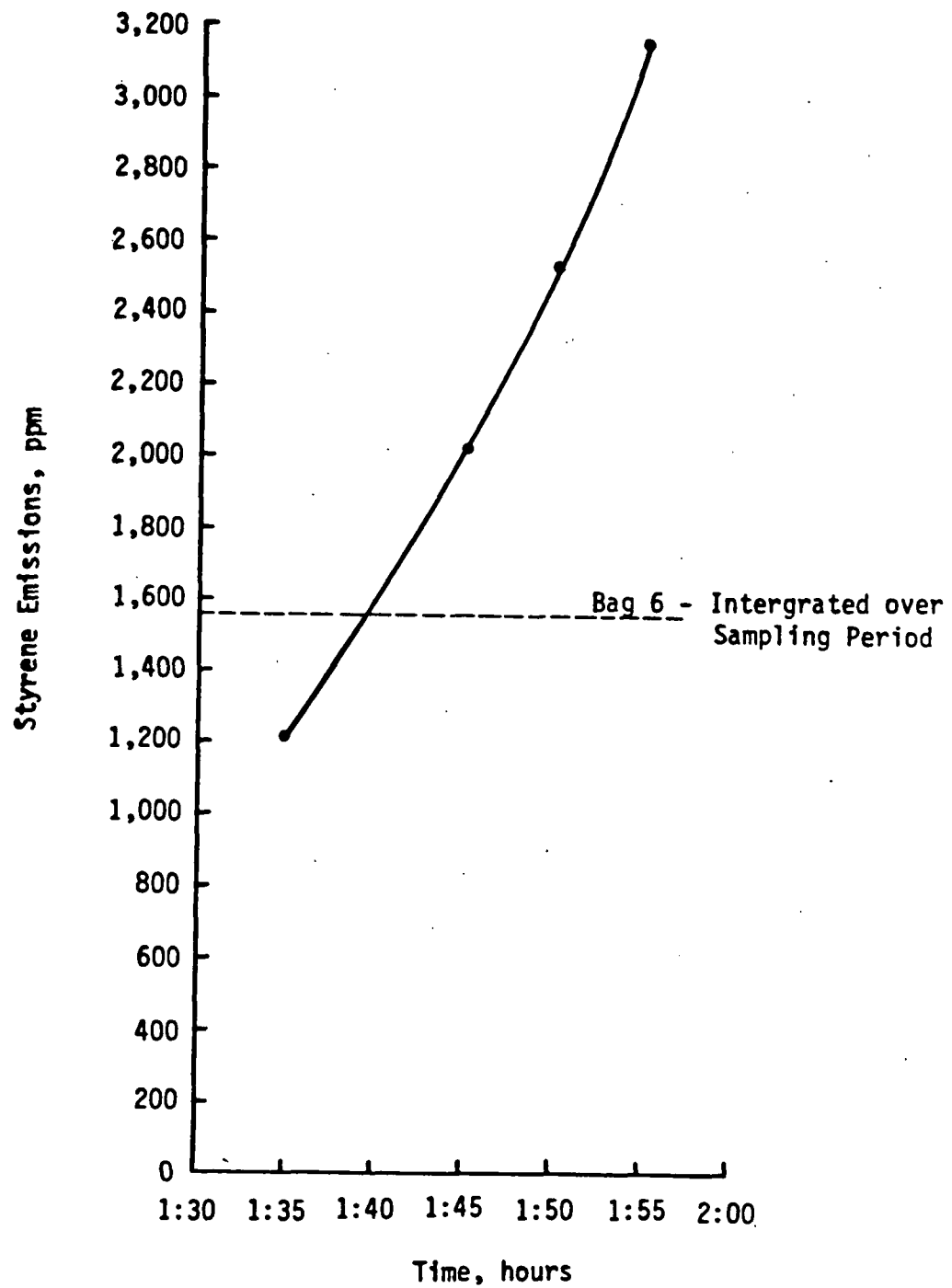


Figure 3-5. Styrene Emissions

4. PROCESS DESCRIPTION

The General Tire plant in Mogadore, Ohio, produces styrene butadiene rubber latex for paper, textile coating, and other uses. The process and equipment used in this production are described below. A process flow diagram and plant layout are shown at the end of this description (Figure 4-1 and Figure 4-2).

The process has three major steps: reaction, blowdown, and stripping. In the reaction step, styrene, butadiene, and small amounts of other monomers are added to a water solution of soap, catalysts, modifiers, and other chemicals and reacted to form SBR latex. The Mogadore plant has several stirred tank reactors for SBR latex use, each about 6000 gallons in size with water jacketing for cooling. The reactions are batch run and take 8 to 16 hours. Completion of reaction is determined by time of reaction and amount of heat removed. The reaction sequencing, including monomer addition, temperature profiles, reacting time and cooling rates, are computer controlled.

After the completion of each reaction batch, the reactors are dumped into a blowdown tank for removal of residual monomer. The Mogadore plant has four blowdown tanks, each able to receive a dump from any of the reactors. During a cycle on a blowdown tank, the tank receives three reactor batches over a 2 to 6-hour period. During this period, monomers are flashed off using vacuum from a central vacuum system. After all three batches are dumped, steam, nitrogen, and vacuum are used to further remove residual monomers from the latex in the blowdown tank. Steaming time and analysis of latex samples are used to determine completion of blowdown. The latex is then pumped from the blowdown tank through shaker screens for removal of coagulated rubber, and then to storage in which the final step is stripping. The residual

styrene content of the latex is brought to within production specifications using a four-stage process involving cyclone separation and vacuum steaming. In this process, steam and latex are combined and pumped into a cyclone, where the heat from the steam and expansion into the vacuum drive off styrene. The latex spins out to the side of the vessel and drains out, where it is preheated, mixed again with steam and pumped into the next stage cyclone. The overhead vapors are cooled to condense out water and pulled out by a separate vacuum pump.

Process monitoring data and plant charts are provided in Appendix D. They present the timing of the process during testing; also, the vacuum and temperature profiles of the central vacuum system on test days.

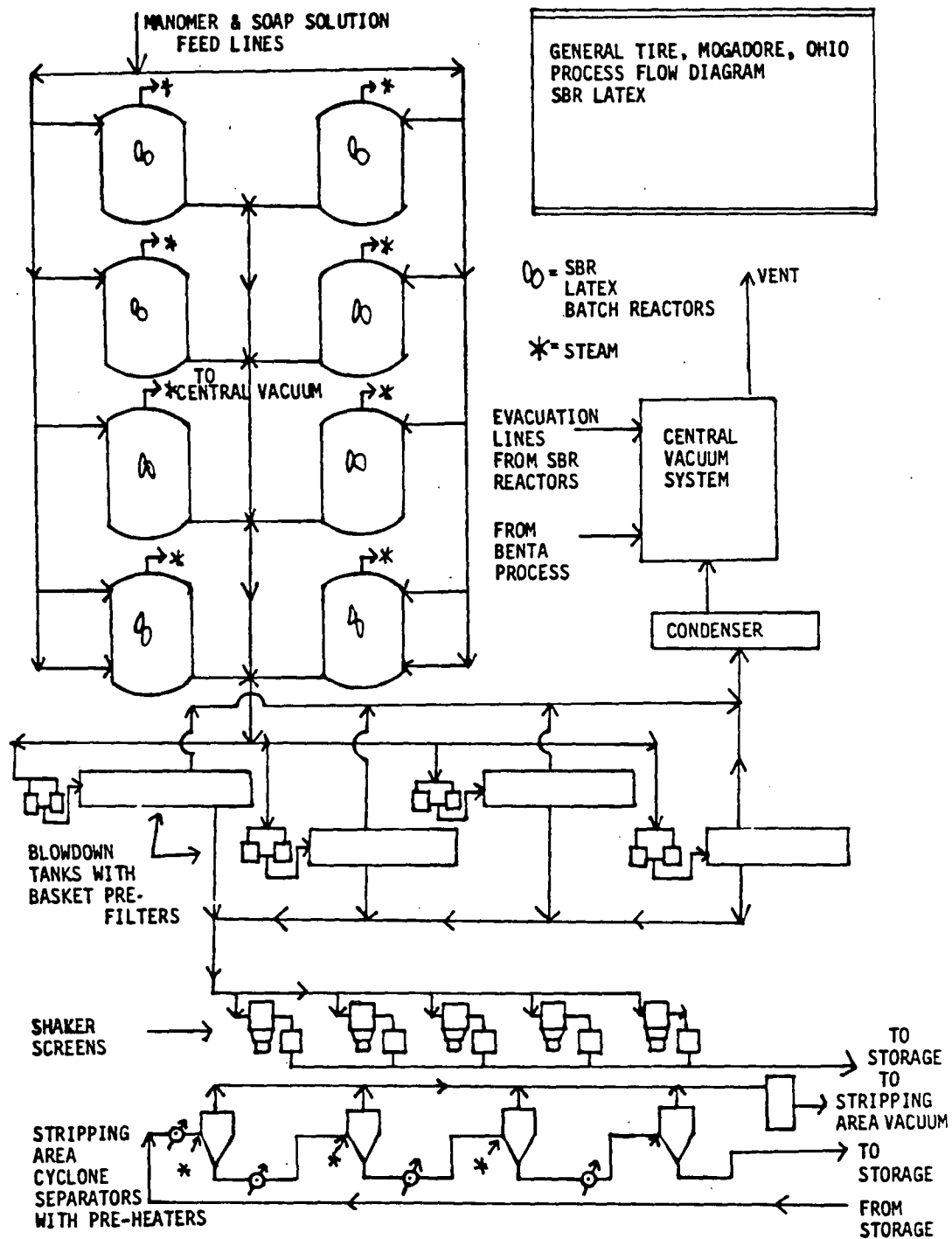


Figure 4-1. Process Flow Diagram

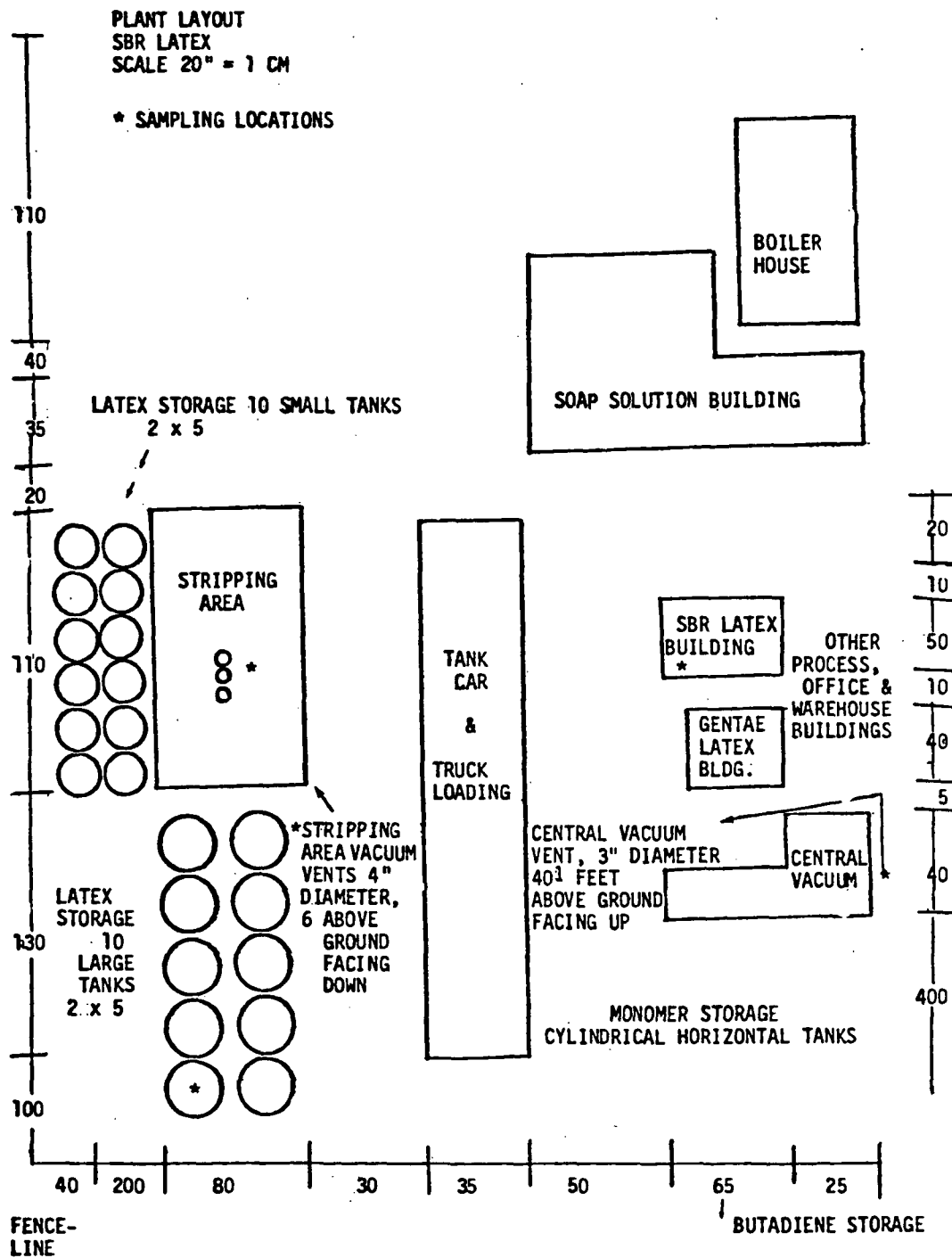


Figure 4-2. Plant Layout

5. SAMPLE LOCATIONS

This section of the report describes the location of the sample points in the styrene/butadiene rubber process tested at the General Tire and Rubber facility. The sample points locations in the process will be divided into five primary areas.

- 5.1 - Reactor blowdown tank system (BDT #4)
- 5.2 - Central vacuum system (CVS)
- 5.3 - Styrene stripper system (SSS)
- 5.4 - Product storage tanks (PST)
- 5.5 - Shaker screens

A brief discussion of the process occurring at these areas will be presented with the relationship to the sample points. A complete discussion of the areas in the process is presented in Section 4. The labeling scheme for the sample location is presented in the glossary and the plant layout with sample locations is presented in Figure 2-1. The sample acquisition method and timing of process will be presented in this section, and the complete procedure discussed in Section 6.

5.1 REACTOR BLOWDOWN TANK SYSTEM (BDT #4)

The reactor/blowdown tank system process is initiated at the reactor. The highly volatile styrene/butadiene formulae is processed from the reactors into a blowdown tank (blowdown tank #4 studied in his test). The gaseous emissions from this processing step are vented to the central vacuum system for emissions into the atmosphere. Sample locations were maintained at the exiting gas vent to the central vacuum system (sample location 1A) to obtain the gaseous emissions, and a latex sample was obtained from a sampling valve of the reactor dumping into the blowdown tank (sample position 4) to obtain the latex product

constituents at this point in the process. The latex formulae is held in the blowdown tank until three reactors have dumped in the tank and had a degassing period of the blended formulae. The latex from the blowdown tank is processed to the shaker screen system. A latex sample location is maintained at the exit of the blowdown tank (sample point 5) from a plant product sampling valve. The latex is analyzed for chemical constituents that have not combined into the product.

Figure 5-1 is a side view indicating the arrangement of major components of the reactor/blowdown system, including the reactor's vessel, blowdown tank, condenser, and approximately locations of the latex and gaseous sampling points. Figure 5-2 is the sample point location at the gaseous emissions from the blowdown tank. This sample point is labeled 1A because the location is a modification of sample point 1 at the central vacuum system. This modification was to provide a more accurate gaseous emission analysis from the blowdown tank emissions before processing through a condenser in-line to the central vacuum system. Figure 5-3 is a layout of the second floor of the reactor building indicating the relationship between the reactors, the blowdown tank (BDT #4) and sample position set-up. Figure 5-4 is a schematic of the sample train utilized at sample position 1A. Figure 5-5 specifies the dimensions of the blowdown tank and components.

The gas stream at position 1A was monitored by a continuous FID and the modified EPA Method 110 was utilized in obtaining an integrated bag sample for GC/FID analyses. The latex samples were taken and prepared according to the sampling procedures from the integrated grab method presented in Appendix G.

5.1.1 Sampling Dimensions Around the Reactor/Blowdown System

The temperature of the blowdown tank exhaust was measured with a plant-installed dial thermometer at the point of the pipe tap used for the blowdown tank exhaust vapor (Point 1). The tap was a one-inch (1") diameter pipe threaded into a 12-inch (12") diameter pipe. The tap was located ten (10) equivalent diameters (E_D) from downstream flow disturbance and two (2) equivalent diameters (E_D) from the upstream flow disturbance. The tap was installed in the top of the 12-inch main,

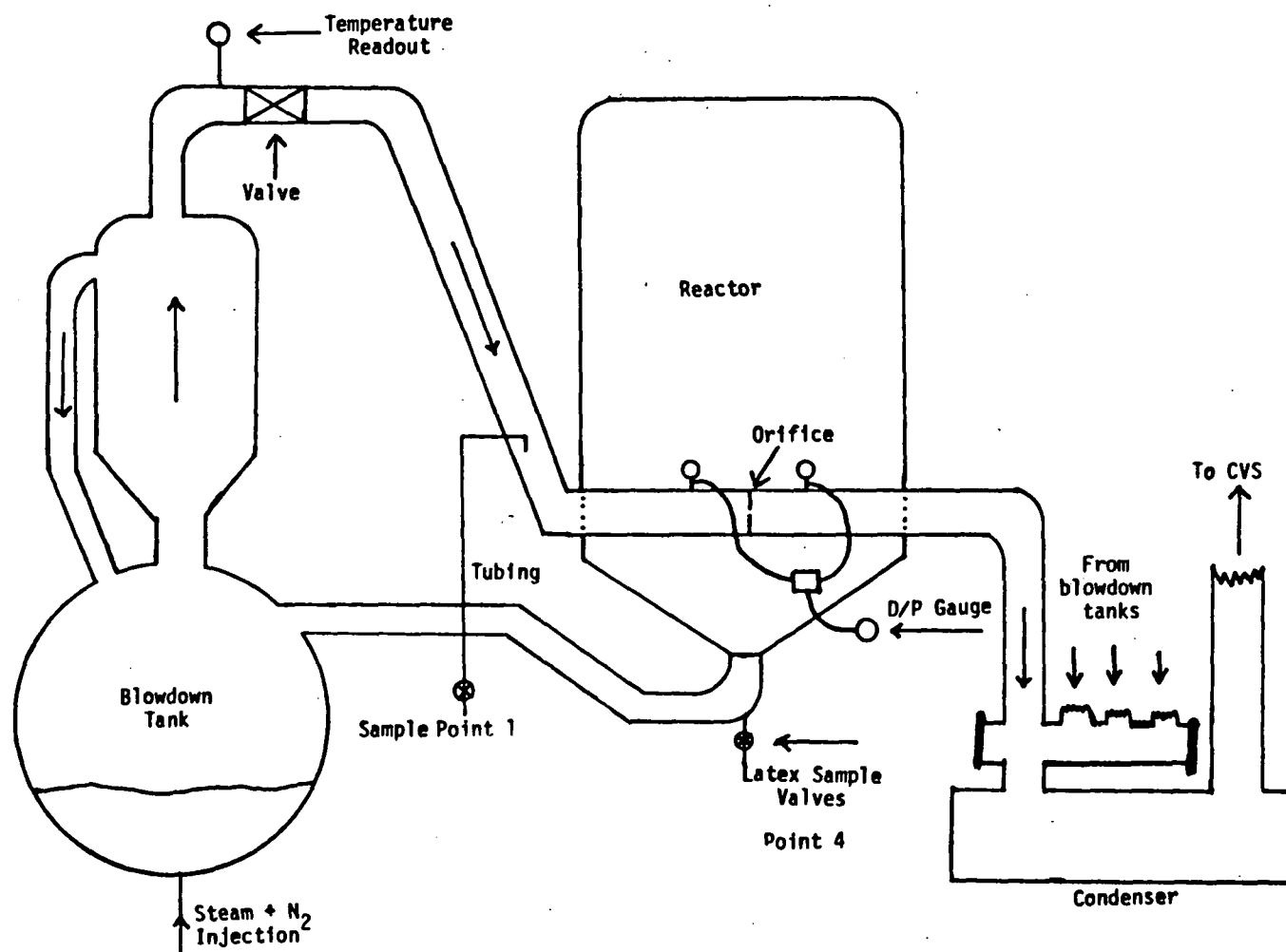


Figure 5-1. Rx/Blowdown System Schematic

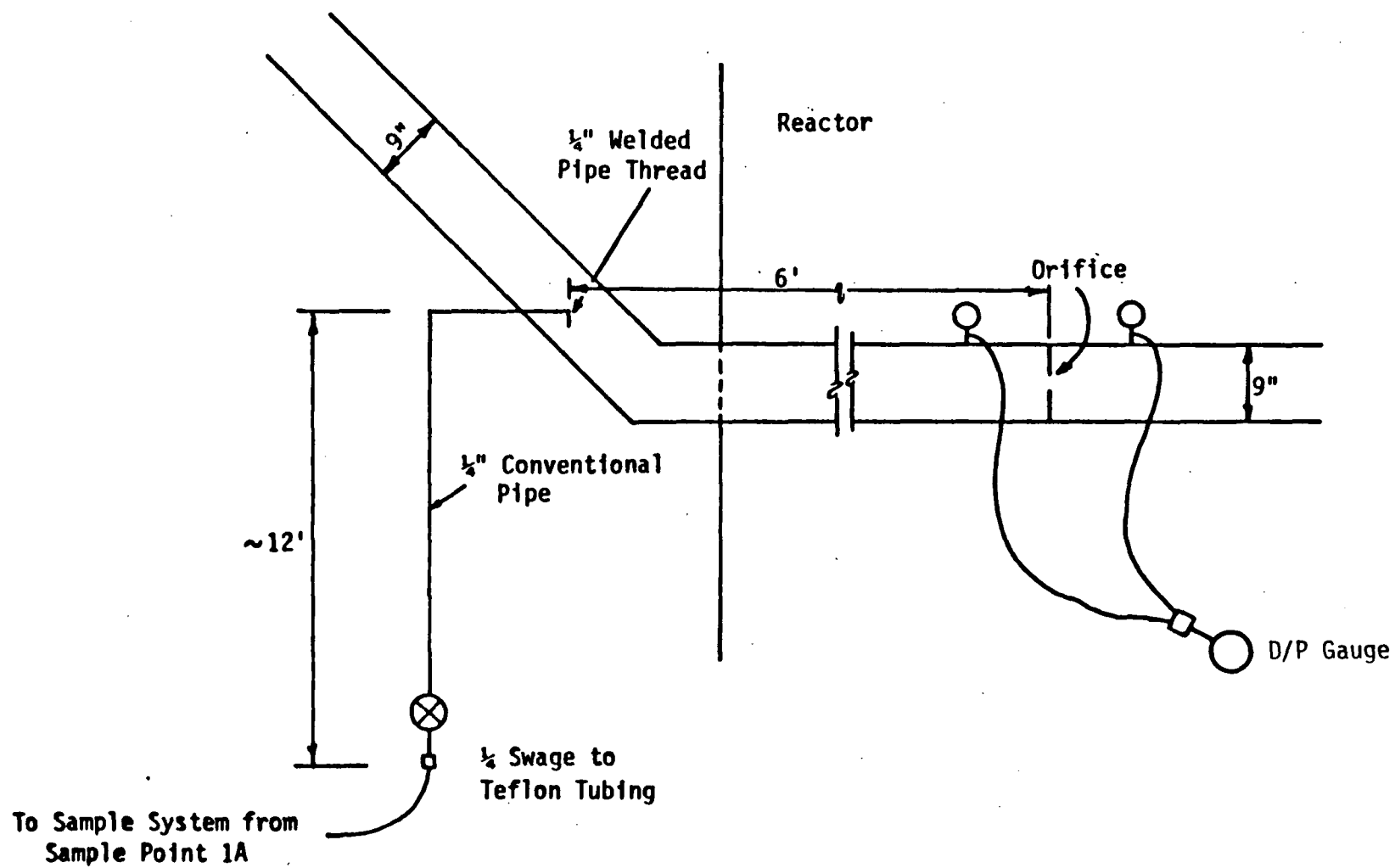


Figure 5-2. Rx/Blowdown Tank Outlet -
Sample Point Location 1A

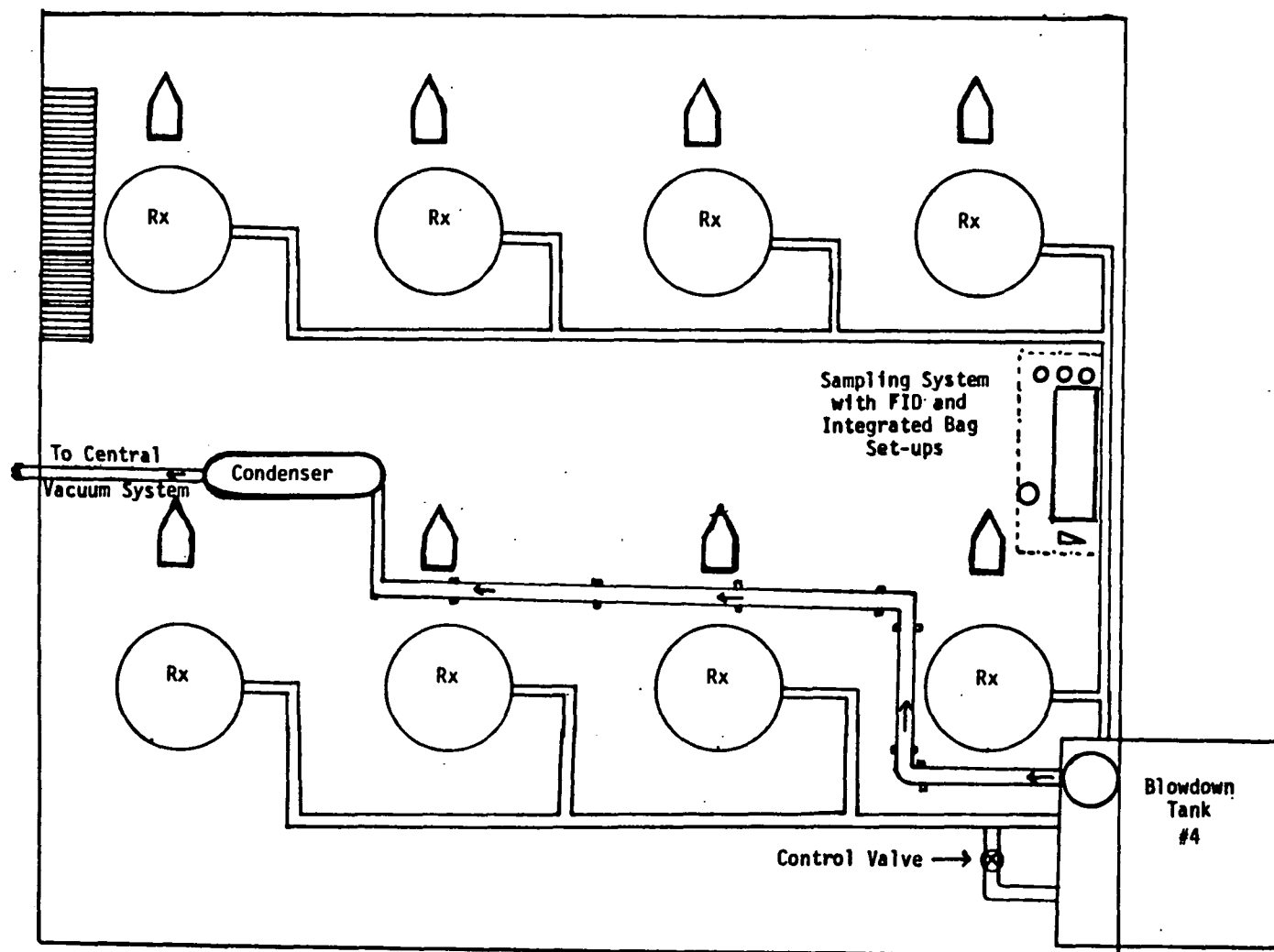


Figure 5-3. Rx/Blowdown Building Schematic (Plan View)

which was 13 feet above the floor level. A 22-foot long $\frac{1}{4}$ " Teflon[®] line connected the 1-inch line to the sampling train. Due to safety considerations, the sampling train equipment was positioned adjacent to building ventilation doors. The area required a hot work permit, which plant safety personnel provided daily after inspection of the area.

The flowrate of blowdown tank exhaust was measured through the use of an orifice. The orifice was installed 12 feet downstream from the sampling tap and 10 feet upstream from the nearest flow disturbance. The orifice was installed at the flange of the 12-inch line and had a nominal diameter of 1 inch.¹ Pipe taps for the orifice measurement were located approximately 30 inches upstream and eight pipe diameters downstream of the orifice. The positioning of the taps was specified by the plant engineer according to standard practices.² Each pipe tap was equipped with a pressure gauge with a line from each pipe leading to a differential pressure (D_p) instrument. The instrument was a model 13A-1 supplied by Foxboro Instrument. The D_p cell (0-150" H_2O) was constructed of 316 stainless steel with a 15 psi working pressure and monitored by a gauge (Moore Products Company), calibrated by plant personnel for 0 to 100 percent of D_p scale.

Two changes were initiated in the blowdown tank flow measurement system during the test program. The blowdown tank developed increased temperature and pressure and the operating pressure of the D_p cell exceeded 15 psi after 2 days of measurements. These conditions indicated a restriction in the orifice and, therefore, it was replaced with a second orifice, which had a 2-inch nominal diameter. Secondly, the pressure gauges installed in the orifice pipe tap were replaced with vacuum gauges, which were required since the pressure of the system was negative.

5.1.2 Sample Procedures at the Reactor/Blowdown Tank System

The sampling train was modified to minimize problems that arose with the condensation of moisture, the maintenance of sample pressure, and adequate dilution of sample of hydrocarbon analysis. The modifications are shown in Figure 5-4.

¹3/26/80 and 3/27/80.

²Derived from Industrial Instruments, pg. 206.

Several pumps were used to provide adequate working pressure to the system. The most effective pump was a Duo-Seal vacuum pump. Because of heat buildup, the pump gradually lost the ability to maintain sample flow against the vacuum of the blowdown tank exhaust. The pump oil was periodically changed to minimize the problem. A quality control check was implemented to compare the effect of the pump on sample integrity by taking gaseous grab bag samples before and after the pump. The results showed no addition or subreactions of hydrocarbons from the pump.

A series of condensers were added in an attempt to simulate the condenser of the blowdown tank exhaust system. A condensate sample from the BDT condenser system was not collected because the BDT condenser was common to all four blowdown tanks at the plant. Two condensers were placed prior to the pump to provide sufficient volume for the condensate collected during the sampling period. The volume of these condensers proved to be inadequate, particularly during the degassing stage of blowdown tank operation. Therefore, the condenser bottles were changed as necessary. A third condenser was placed after the pump to guard against condensation of the vapor due to system pressure restriction.

Throughout the testing at this location difficulty was encountered in supplying adequate sample pressure to all components of the sampling train. The hydrocarbon component of the sampling stream required extensive dilution with N_2 before analysis. Sample flow to the dilution board was monitored with a rotometer to insure accurate dilution. The dilution board was calibrated before and after field testing and is described in Appendix H. The flows to the integrated bag and hydrocarbon analyzer were monitored with flowmeters and were maintained at 2.0 liters per minute and between .2 and .5 liters per minute, respectively. Any excess sample pressure was removed at the point of attachment of the grab bag (see Figure 5-4).

The latex samples were taken directly from sample valves utilized by the General Tire personnel to sample the product at the different stages in the process. The preparation of the sample bottles was performed beforehand in the field lab. The TBC solution was added to the appropriate sample bottle and labeled. The sample position 4 sample

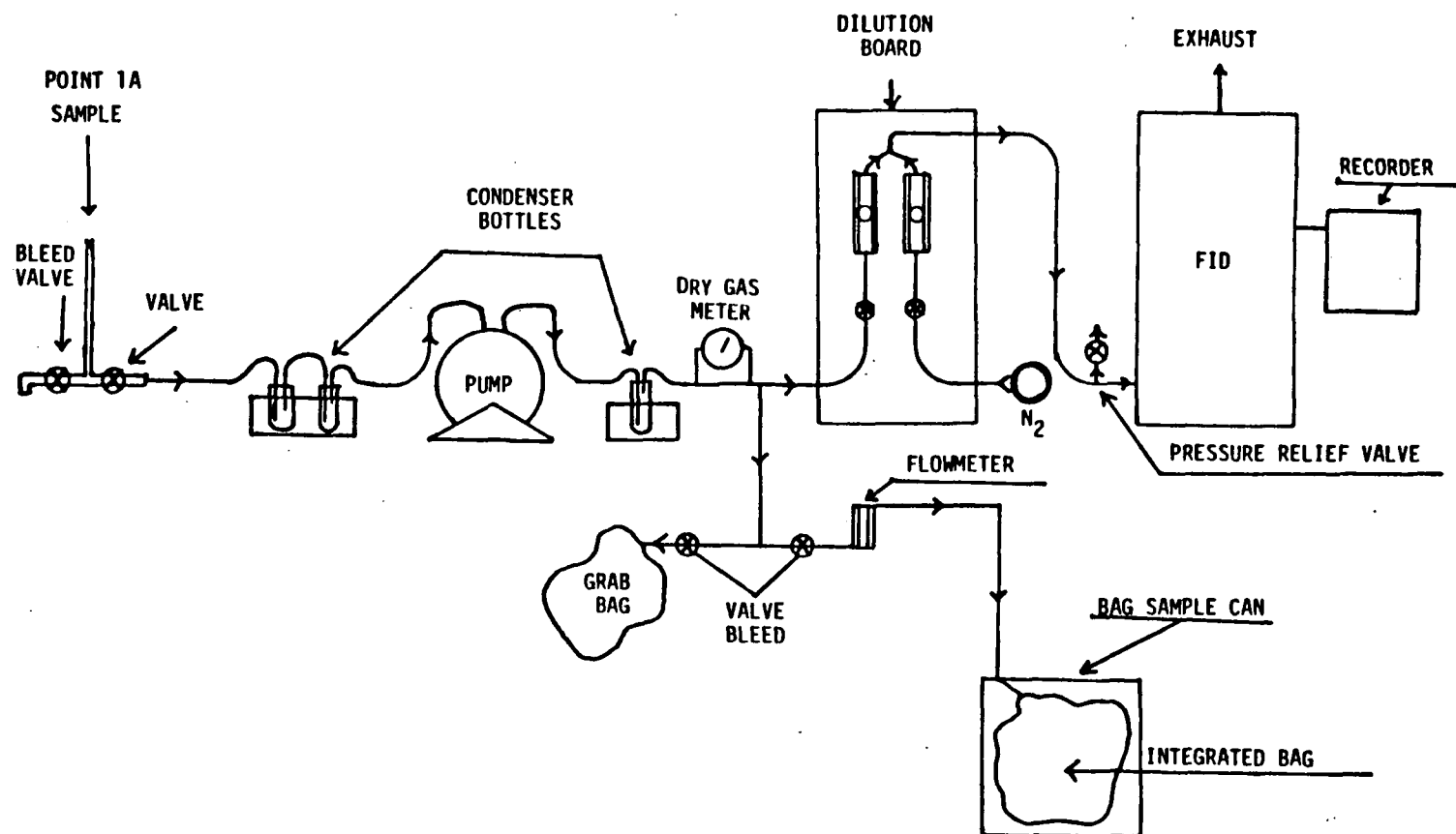


Figure 5-4. Sample Train Schematic

Figure 5-5. Blowdown Tank #4

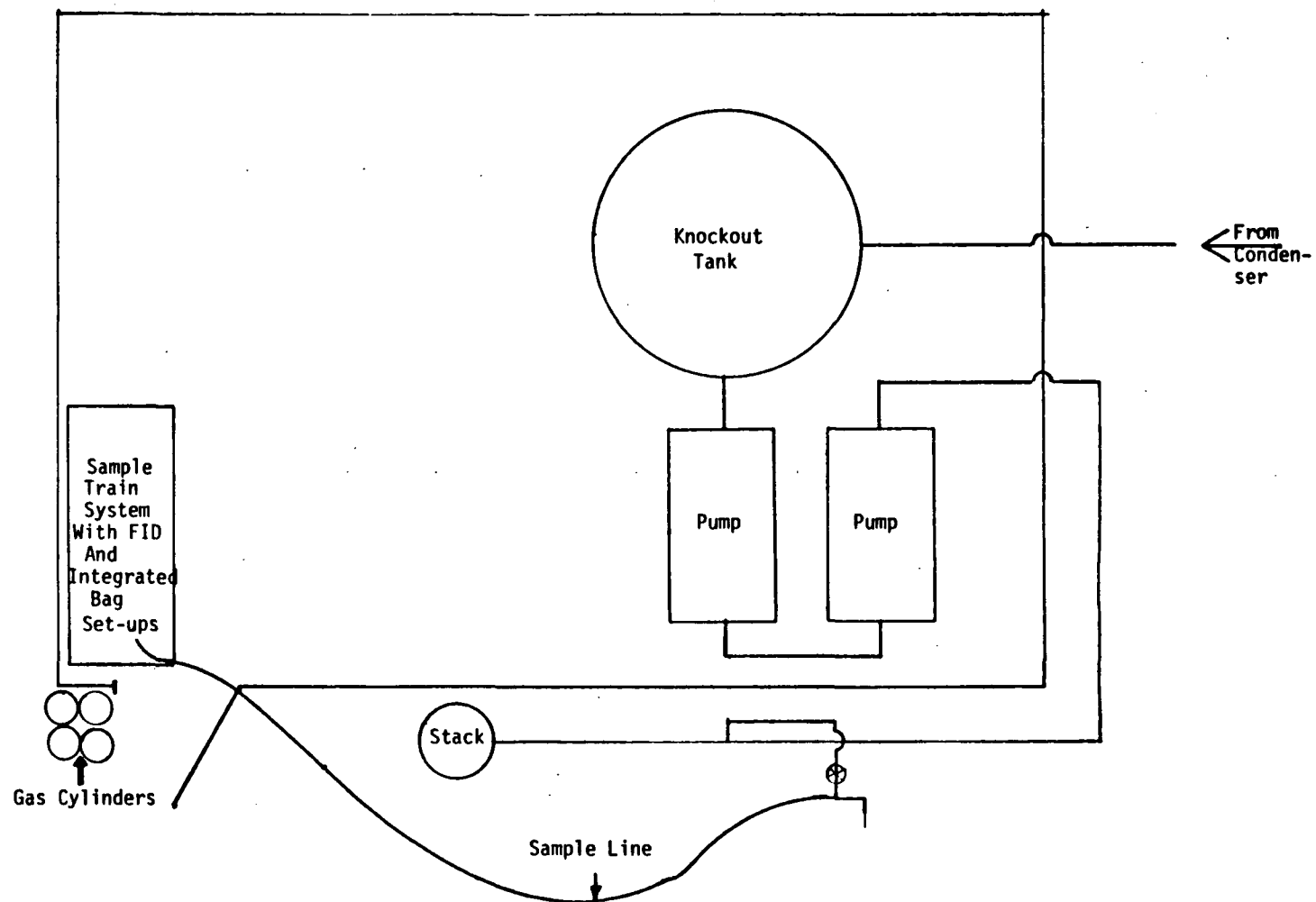


Figure 5-6. Central Vacuum System (Floor Plan View)

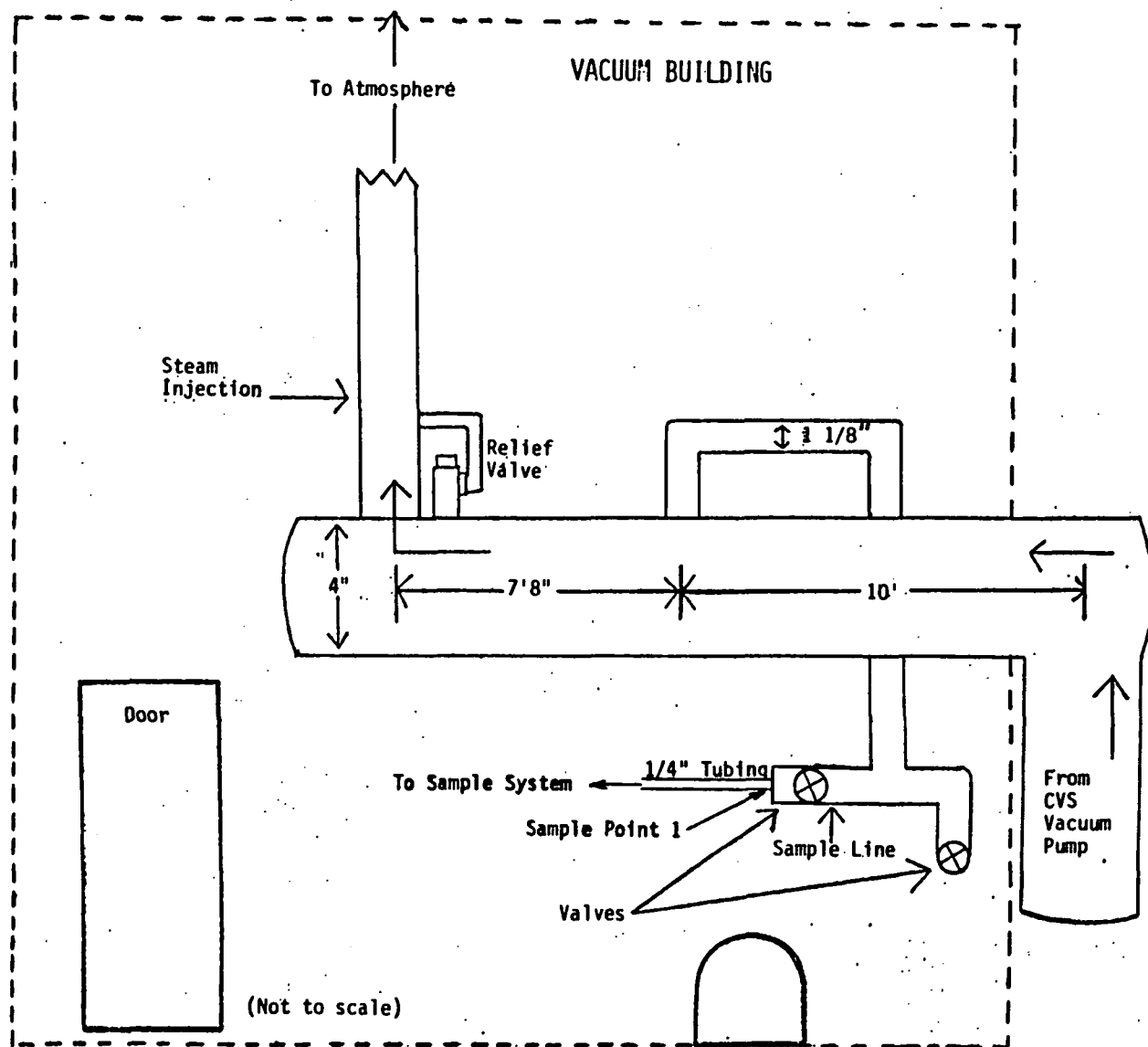


Figure 5-7. Central Vacuum System - Exhaust Piping: Sample Point #1

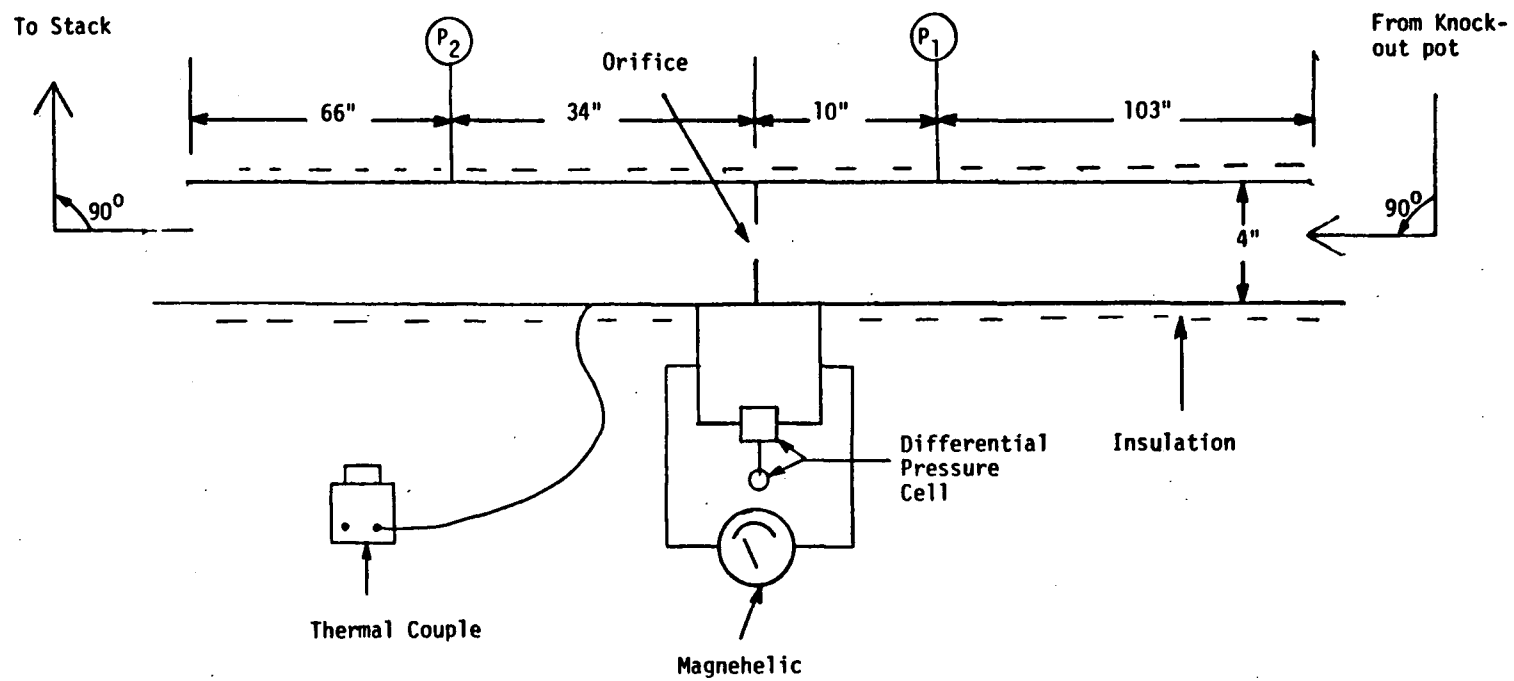


Figure 5-8. Vacuum System Flow Measurement (Side View)

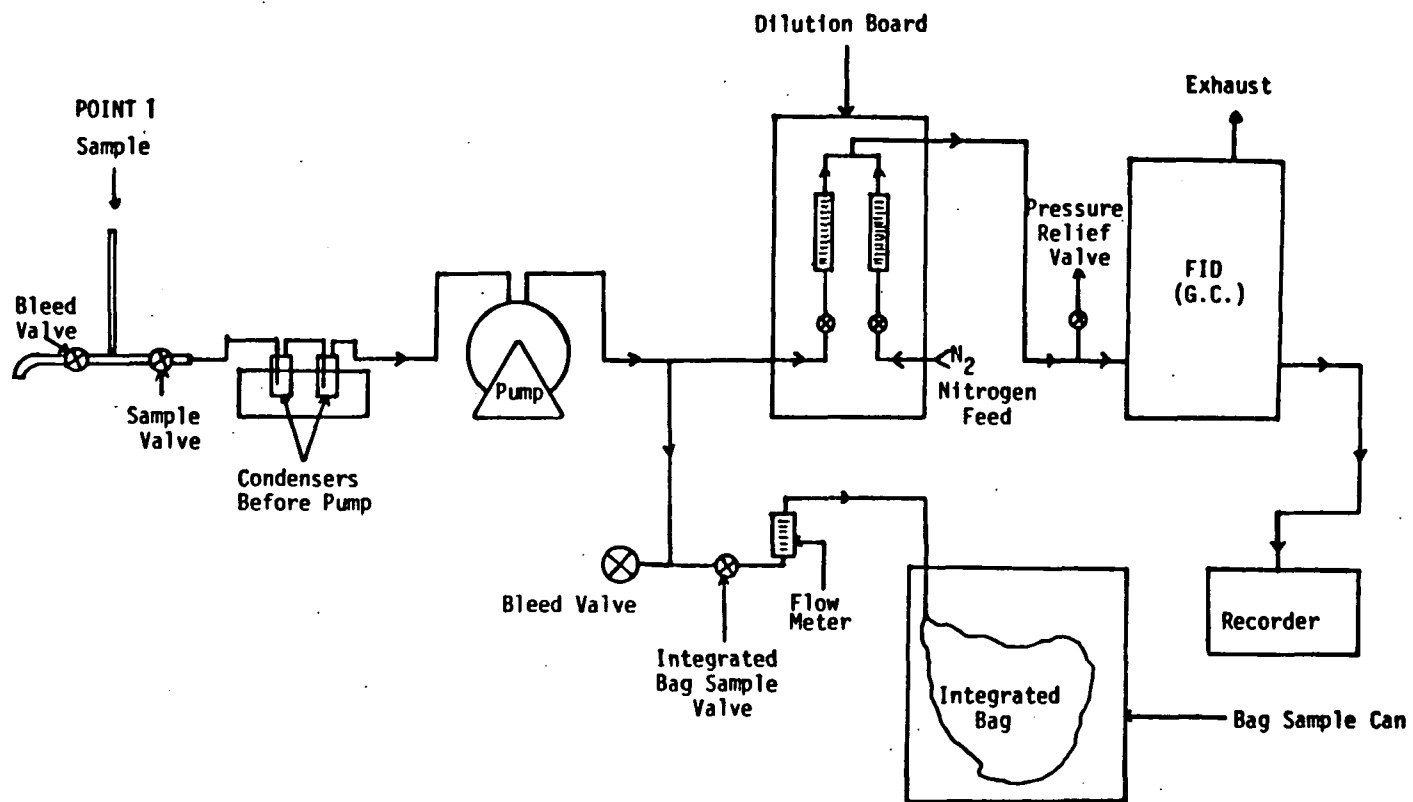


Figure 5-9. CVS Sample Train Schematic (Point #1)

was obtained from the reactor dumping into the blowdown tank. The temperature of the sample was taken with a metal thermometer directly from the sample bottle. The sample position 5 (Figure 5-5) latex was sampled after the degassing period of the blowdown tank, and the latex from the blowdown tank was being processed to the shaker screens.

5.2 CENTRAL VACUUM SYSTEM (CVS)

The central vacuum system is maintained as an outlet for the process gas emissions. The system pulls the gas emissions from the blowdown tank system through a condenser to the CVS. The CVS contains a knockout tank as a control device before emitting the gas stream through a stack to the atmosphere. A gas sample location was maintained after the gas stream had been processed through the CVS and before the stream is vented to the stack (sample point 1). The gas stream at point 1 was sampled by a continuous monitor FID for total hydrocarbons, and the modified EPA Method 110 was utilized in obtaining an integrated bag sample for GC/FID analyses.

Figure 5-6 is a plan view schematic of the central vacuum system (CVS). Figure 5-7 is a side view schematic of the central vacuum system indicating the sample point. Figure 5-8 shows the arrangement of the flow measurement equipment prior to the CVS sample acquisition point. Figure 5-9 is a diagram of the sample train used to quantify the VOC emission rate to the atmosphere from the central vacuum system.

5.2.1 Sampling Dimensions at the Central Vacuum System

The sample acquisition from the CVS was taken from the 4-inch line exiting the central vacuum system. Positive pressure was encountered at the points of sample acquisition and flow measurement. A 1 1/8" pipe was tapped into the 4-inch exhaust line to provide an easier sampling point. The tap was equipped with valves to regulate the amount of sample desired. The exhaust line (4") from the CVS was partially insulated and, therefore, in order to maintain sample integrity, the 1 1/8" line was also wrapped with insulation to prevent excess condensation. The sample point was 30 equivalent diameters downstream from the nearest flow disturbance. Steam was injected into the 4-inch line approximately 8 feet after the sample point.

The flow rate of the flue gas from the central vacuum system was measured prior to the sample point by pressure differential across a known orifice which was installed approximately 28 equivalent duct diameters downstream from the nearest flow disturbance and approximately 25 equivalent duct diameters upstream from the nearest flow disturbance. The orifice had a nominal diameter of 1 inch during the first week of testing¹ and a 2-inch nominal diameter during the second week of testing. The pressure gages installed in the pipe upstream and downstream from the orifice (P_1 and P_2 , respectively) were connected to the D_p instrument, similar in design to the instrument utilized at the blowdown tank flow measurement site. Because of the low pressure differential across the D_p cell, a magnehelic (0" - 10" of water) was installed in line with the D_p cell to monitor changes in the flow profile at low flow conditions.

5.2.2 Sampling Procedures at the Central Vacuum System

The sampling activities at the central vacuum system operated without any major disruptions. A few miscellaneous notations, however, are in order. The sampling conducted on 3/27/80 was conducted by the integrated bag - evacuated can method only. Total mass emissions to the atmosphere monitored by the FID hydrocarbon analyzer were determined only during the second week of testing.

The plant recorded both the central vacuum system temperature and vacuum of the system at the vacuum pumps inside the CVS building. This data was not identified as being available during the actual testing period. However, examples of CVS temperature and vacuum are included in the process description appendix. For testing purposes (flow measurement), the temperature of the flue gas was measured with a type K thermocouple wire against the outside of the 4-inch exhaust pipe. The temperature was within $\pm 5^\circ\text{F}$ from the plant's measurement system.

5.3 STYRENE STRIPPER SYSTEM (SSS)

The latex stream from the pre-blend tank is processed through the styrene stripper system. The gas emissions from the stripping process

3/26 and 3/27.

were vented to the atmosphere (sample point 2). The efficiency of the stripper system was determined by sampling the latex at the inlet (sample point 8) and at the outlet (sample point 9).

Figure 5-10 is a functional diagram of the styrene stripper system. The SSS used steam to strip residual styrene out of the latex. The vapor stripped from the latex is pulled under vacuum to a water-cooled condenser (Figure 5-11). The cooled exhaust is pulled under vacuum from the condenser to the styrene vacuum pump from which the exhaust gas is vented to the atmosphere. Figure 5-12 is a schematic of the sample train utilized to measure the atmospheric emissions from the styrene stripper system exhaust (sample point 6).

The hydrocarbon emissions to the atmosphere were determined by continuous monitoring with the Horiba hydrocarbon analyzer on 4/2/80. Integrated bag samples (3) were taken by the modified EPA Method 110 to quantify the individual components of the gas stream. Analysis of the bag samples was by GC/FID. The inlet latex and the outlet latex were sampled by the latex grab method (Appendix H), three (3) times during the SSS exhaust monitoring. The condensate from the condenser could not be sampled because of dilution with city water.

5.3.1 Sampling Procedures at the Styrene Stripper System

The inlet latex samples were taken from the product level tank (Figure 5-10) by dipping with the sample bottle. Temperatures of the system were checked at each of the vapor liquid separators, the condenser vapor exhaust, and the condenser water inlet. The vacuum of the system was monitored prior to and after the condenser. The outlet latex sample was taken after the fourth stage pump from a sample valve. The latex sample was sampled according to the standard procedure (Appendix H). The latex at this point was pumped to the final product storage tank. The system exhaust was measured for VOC concentration and flow at sample point 2. This point was located outside the filter building, approximately 8 feet above the ground. For sampling purposes, a flexible exhaust hose was used to extend the vent to ground level. A vane anemometer was installed in line to measure the volumetric flow. A teflon line was also inserted into the flexible duct to draw out a vapor sample for the sampling train (Figure 5-12).

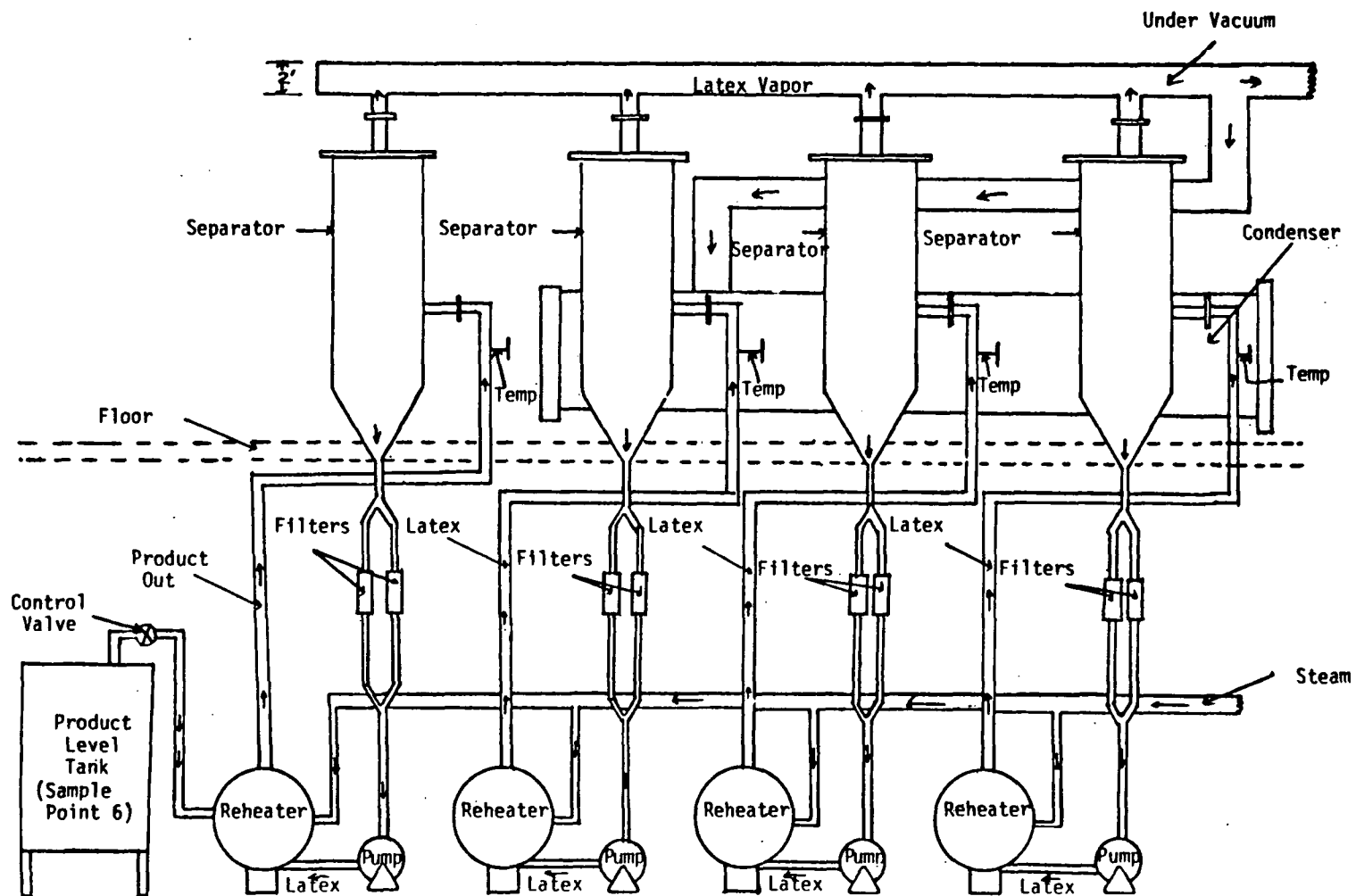


Figure 5-10. Styrene Stripper System Function Diagram

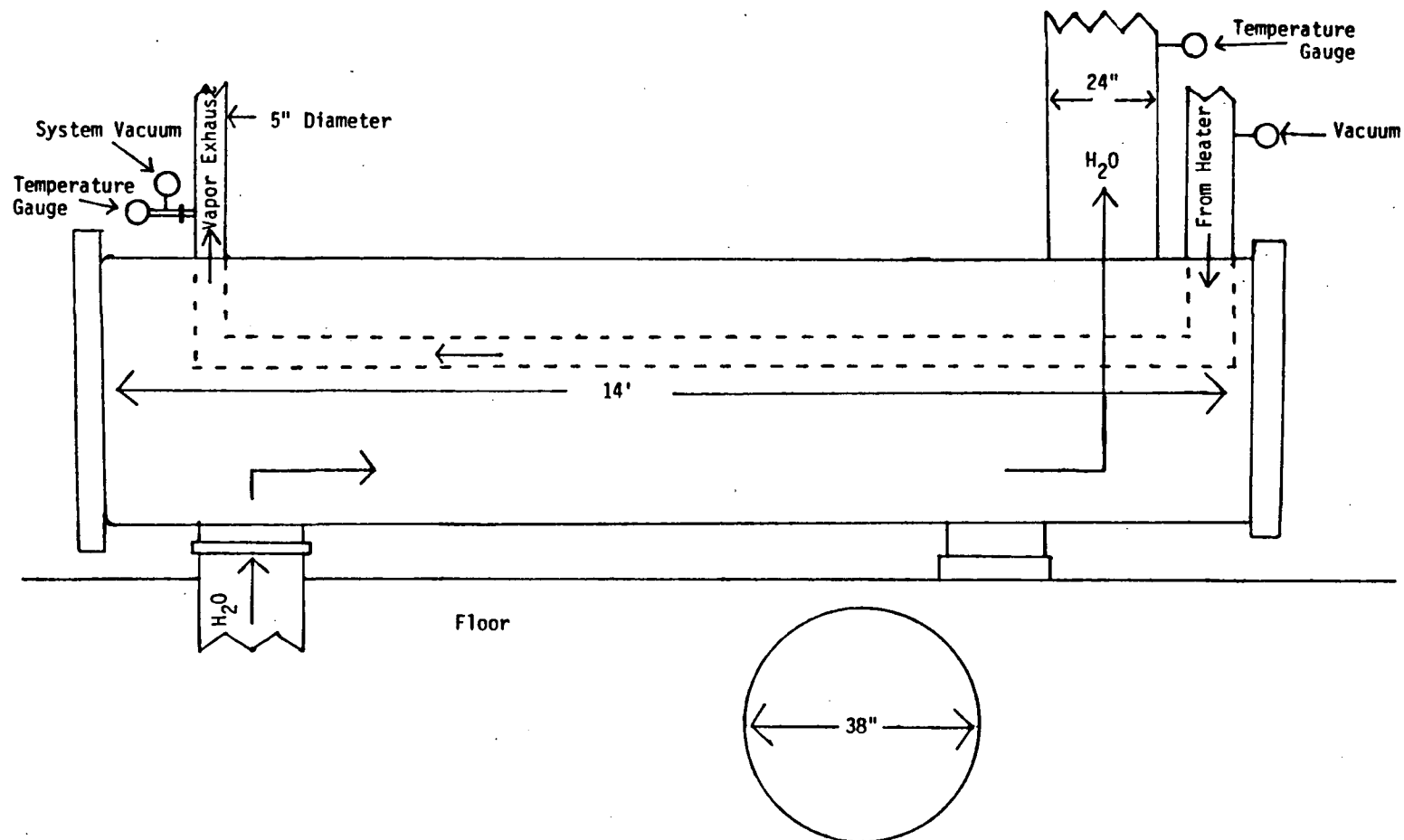


Figure 5-11. Styrene Stripper System Condenser
(Side View)

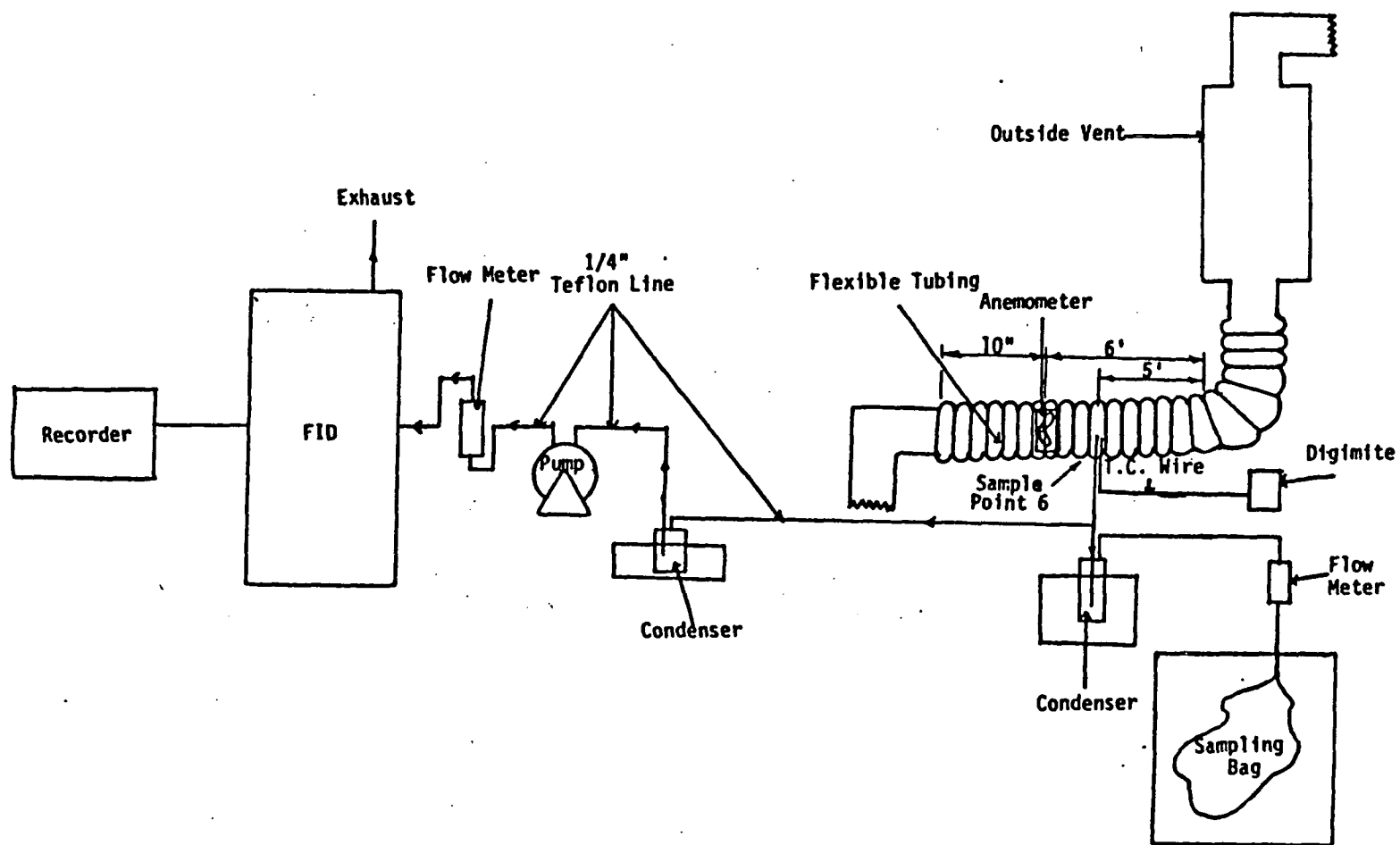


Figure 5-12. Sample Train Styrene Stripper Exhaust - Sample Point #6

Two minor operational problems were encountered during the sampling of the styrene stripper system. The latex inlet sample was taken by dipping from the incoming product line which was plugged with coagulated latex. However, the representativeness of the sample was then judged to be adequate. A condensate sample from the vapor condenser was desired for the purpose of formulating a more complete mass balance determination. However, the system design and operation was such that a condensate sample could not be collected prior to dilution with city water. The amount of dilution was undeterminable and was estimated to be large by the plant process engineer. Therefore, no condensate sample was obtained from the styrene stripper system.

5.4 THE PRODUCT STORAGE TANK (PST)

A product storage tank was sampled to determine gas emissions to the atmosphere (sample point 11) during the filling operation. Tank #39 was sampled during a final product filling operation from the styrene stripper. The hydrocarbon vapors were sampled by the integrated bag method, and the flow of exhaust was measured by a vane anemometer at the tank vent. Figure 5-13 is an aerial view and Figure 5-14 is a side view of the tank. The tank was heated with a steam jacket and was agitated with a mechanical mixer. The gas sample point was maintained 3 feet inside the tank from the headspace of the tank. The point was obtained by inserting the teflon sample line through the tank vent exhaust. The gas integrated bag sample was obtained by the modified EPA Method 110 for analyses for GC/FID.

5.4.1 Sampling Procedures at the Product Storage Tank

Tank #39 was approximately 25' in diameter. The top of the tank was enclosed with a standard safety railing, where the 4-inch diameter tank vent was located. A flexible hose extension was added to the tank vent for the flow measurement. A large capacity dry gas meter was intended to measure the tank flow during filling, but the flow from the vent proved to be below the measuring capacity of the meter. Therefore, a vane anemometer was used to monitor the flow during the second and third integrated bag samples taken at this location on 4/2/80.

Product Mixer

Tank Access-
Measurement Port

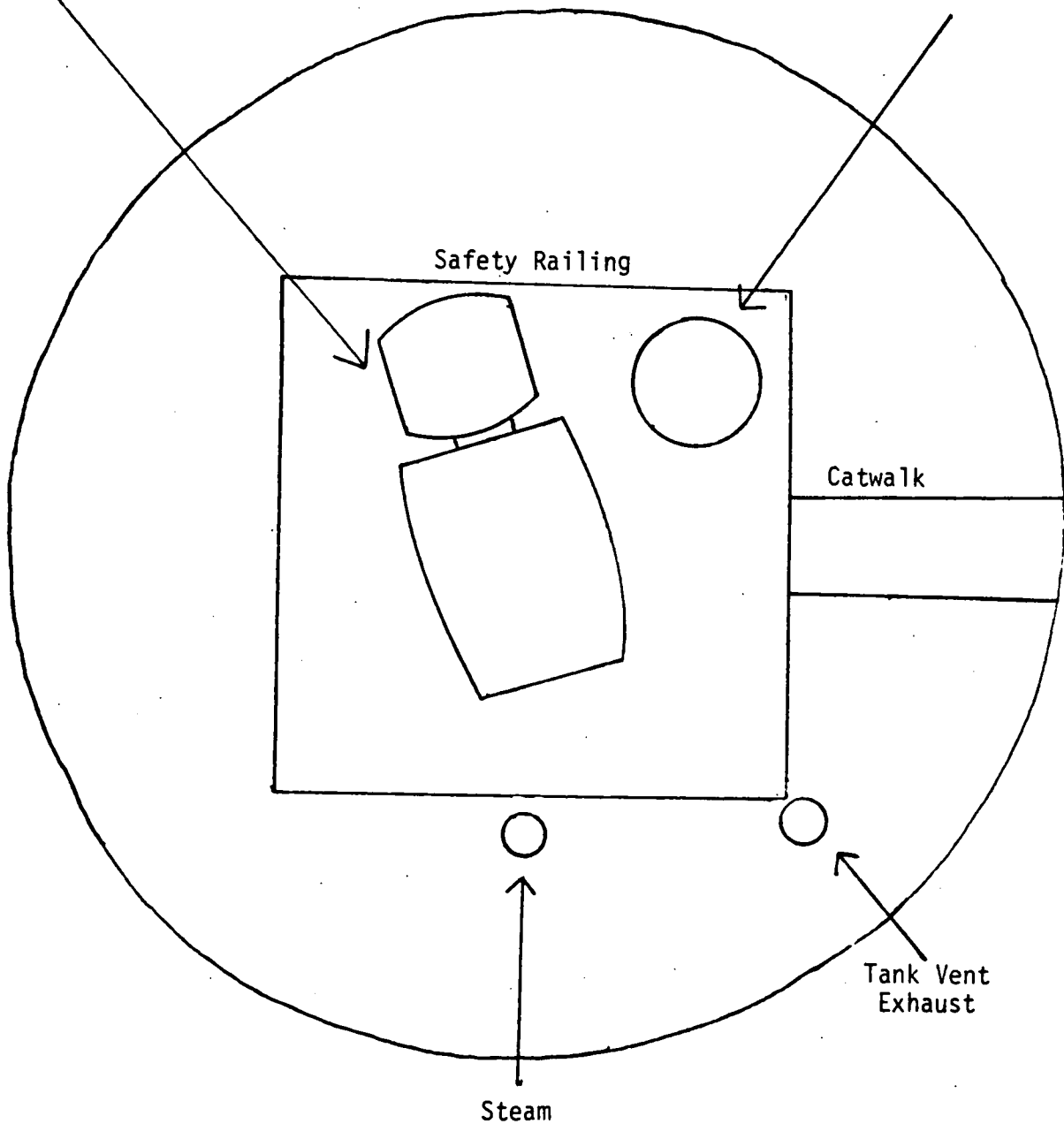


Figure 5-13. Product Storage Tank - Aerial View

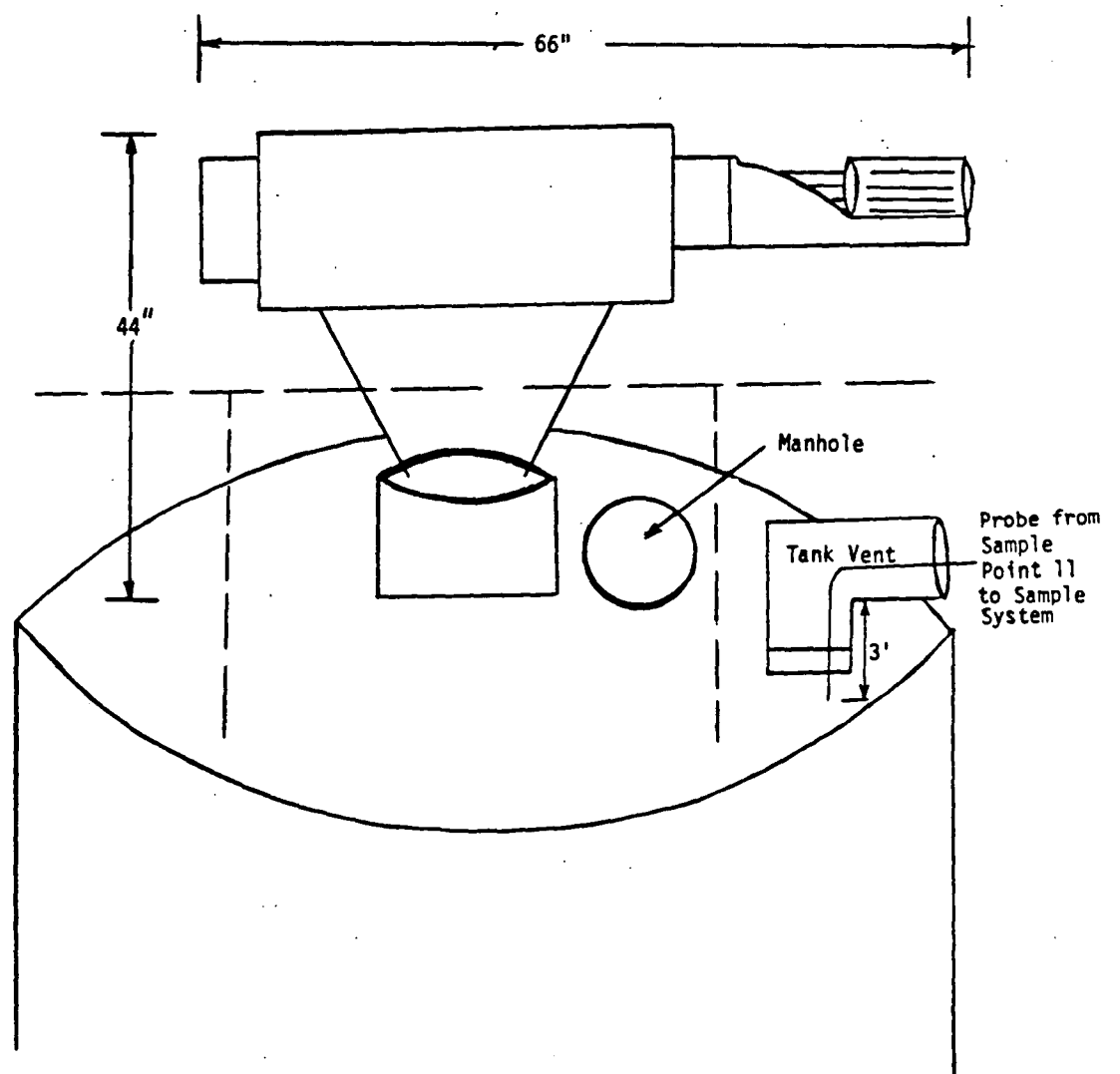


Figure 5-14. Storage Tank: Sample Point #11 (Side View).

The manhole on the top of the tank was fitted with a stainless steel sampling probe and sealed during the bag sampling. Between integrated bag samples, the latex volume of the tank was measured. The manhole was reopened and the level in the tank was measured by a 500-inch tape measure. The tape was read as inches of tank outage, with each inch representing 195 gallons of product. Outside of the flow measurement difficulties during the first integrated bag, no sampling problems were encountered.

5.5 SHAKER SCREENS

The latex stream from the pre-blend tank is processed through a shaker screen system. The coagulated latex is extracted on the screens and disposed of, while the filtered latex is pumped through the system to temporary storage. The gaseous emission from the filtering process (sample point 3) is emitted as a fugitive emission into the process room.

Figure 5-15 is a schematic of a shaker screen and presents the location of sample point 3. Figure 5-16 is a generalized schematic of the shaker screen set in the process before the stripper system. Only one integrated bag sample was taken by the evacuated can method according to the modified EPA Method 110 for analyses by GC/FID. The sample was obtained over the shaker screens during operation. The ambient concentration of styrene was expected to be low.

5.5.1 Sampling Procedures at the Shaker Screens

A stainless steel probe was extended over one of the shaker screens, approximately 20 inches above the first stage of the shaker screen. A 30 minute bag sample was collected with the evaluated can system. Temperature above the shaker screens was measured with a Type K thermocouple attached to the probe assembly. No sampling problems were encountered at this location. Only one bag sample was collected.

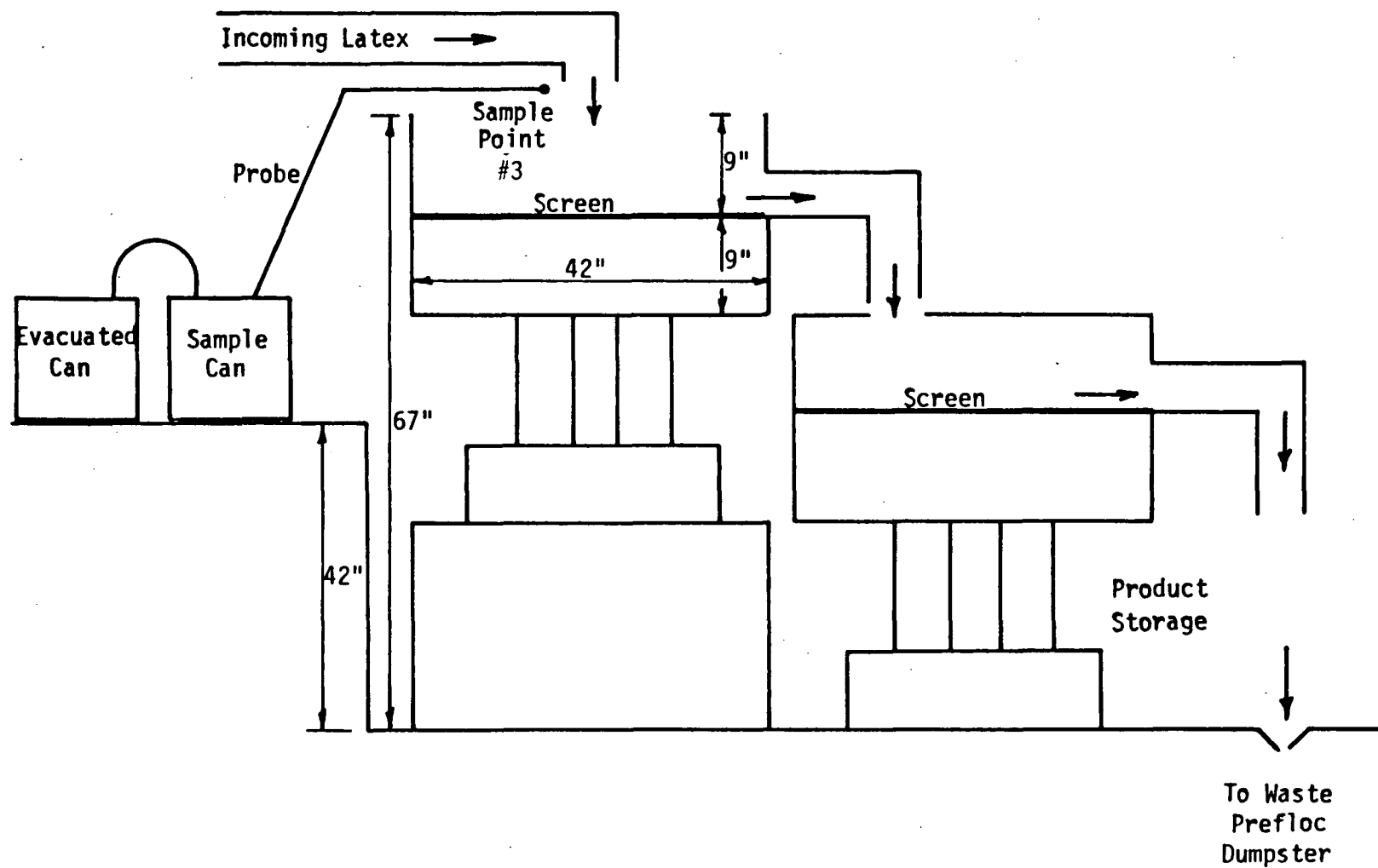


Figure 5-15. Shaker Screens

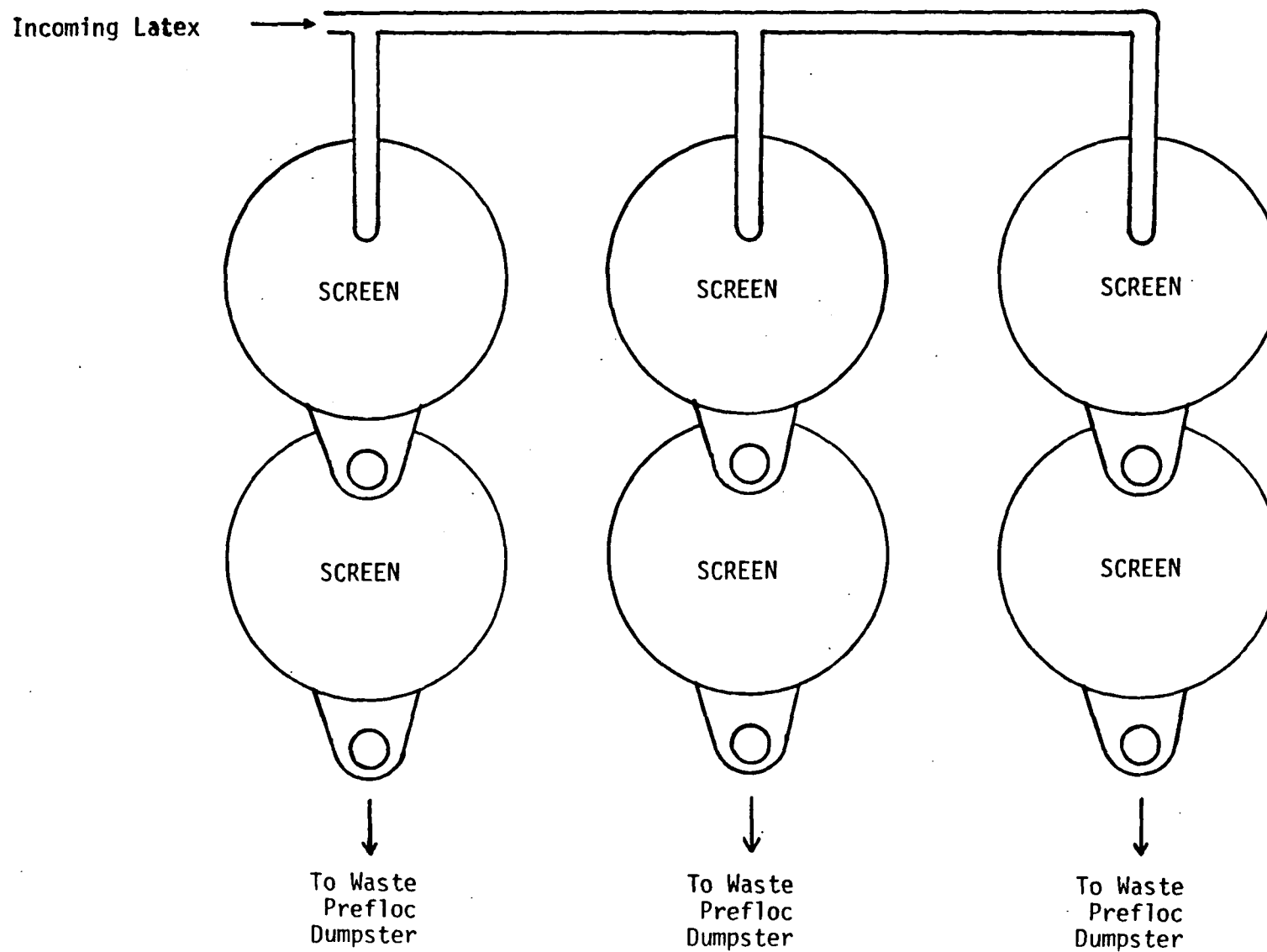


Figure 5-16. Shaker Screens - Plan View - 2nd Floor Level

6. SAMPLING AND ANALYTICAL PROCEDURES

Section 6 discusses all the sampling and analytical procedures applied to all the samples. Modifications of the draft methods are also discussed in depth in this section. The section is divided into four discussions:

Section 6.1 describes the sampling methods used at each sample location.

Section 6.2 describes the analytical procedures used on specific types of samples and types of analysis, for example hydrocarbon and analysis of latex samples by GC/FID.

Section 6.3 discusses the hydrocarbon emission concentrations (determined by continuous monitor FID) in relation to the process as well as a comparison of the FID results and the integrated bag sample results (determined by GC/FID).

Section 6.4 discusses the Quality Assurance and Quality Control measures followed throughout the test as well as the results of a degradation rate study of both the gaseous hydrocarbons and the latex hydrocarbons.

6.1 SAMPLING PROCEDURES

Pertinent data compilation and sample collection provided information for the analysis and characterization of VOC emissions and the efficiency of the control devices in the SBR process. The process data monitored were gas flows, liquid flows, and temperatures. The gas flows were measured with a magnehelic, a vane anemometer, or plant installed standard orifice with differential pressure readouts. The liquid flows obtained from plant GPM meters or tank level readouts. The temperature was monitored with K-type thermocouple wire with temperature

readout or metal thermometers. Moisture determination was not monitored because condensate from sample points were analyzed and found to be liquid hydrocarbons. Gas sample were collected using the integrated bag system with an evacuated can according to the modified EPA Method 110. The gas stream was also continuously monitored with a Horiba OPE-405 hydrocarbon analyzer utilizing flame ionization detection (FID). A dilution board adaption was required at the gas streams with high HC concentration levels. The latex samples were collected using a latex grab collection procedure. Appendix H, Field Sampling Procedures, contains the procedure outlines utilized for the sampling at the Mogadore facility. A following discussion presents the procedures used at each sample location with the adaptations from the method procedures.

6.1.1 Blowdown Tank Gas Outlet, Sample Procedures

This sample location was labeled 1A to denote this location as a modification of sample location 1. This modified sample location allowed the gas stream to be sampled before processing through the condenser in line to the central vacuum system. Sampling modification with condenser bottles was required to eliminate the condensate from the gas stream.

6.1.1.1 Flow Measurements. The flow measurements at the blowdown tank gas outlet were determined with an orifice placed in-line between the BDT #4 outlet and the condenser. The differential pressure gauge was a Foxboro Instrument Model #13A-1 and was installed by the Mogadore personnel. Problems developed during the second test day when liquid formed around the 1-inch orifice originally installed. The restrictions caused error in the differential pressure readout. This problem was overcome by installing a 2-inch orifice.

6.1.1.2 Temperature Measurements. The temperature of the outlet gas stream was monitored from a dial thermometer temperature gauge installed by the plant inline between BDT #4 outlet and the condenser. The temperature gauge was before the orifice as in Figure 5-1. The dial thermometer was not calibrated for accuracy. But the precision of an instrument of this type is approximately $\pm 10^{\circ}\text{F}$.

6.1.1.3 Gas Sampling Procedures. Integrated gas samples and continuous HC monitoring were obtained at the blowdown tank outlet. The gas samples collected utilized the modified EPA Method 110 presented in Appendix H with the evacuated can. The sample system was modified with the dilution board and condenser (Appendix G). The dilution board was calibrated and operated according to the procedure in Appendix H. The condenser bottles were placed before and after the sampling pump. The amount of liquid captured in the condenser bottles was recorded and analyzed. A significant problem occurred during the degassing of the blowdown cycle. The injection of steam into the blowdown tank exceeded the capacity of the condenser bottles. Therefore, the train was shut down numerous times during this cycle to install new condenser bottles. This condensate problem could have caused error in the accuracy of the integrated bag concentration during this cycle because the train was down approximately 12 percent of the steam degassing period.

6.1.2 Blowdown Tank Inlet and Outlet Latex Sample Procedures

The latex flow in and out of BDT #4 was sampled and analyzed for residual styrene concentrations present in the latex at this point of the process. The inlet latex sample (sample position 4) was taken from the product sample valve of the reactor dumping into BDT #4 (Figure 5-1). The outlet latex (sample position 5) flow was obtained from a product sample valve at the BDT #4 before transfer to the shaker screens (Figure 5-5).

6.1.2.1 Flow Measurements. The latex volume flow measurements at the inlet and outlet latex streams of BDT #4 were calculated and recorded by the plant personnel assuming a typical percent completion of the reaction. The total inlet volume flow of latex was based on the sum of the theoretical volume of the three reactors dumping into BDT #4 during the test period. The outlet flow recorded and reported in Appendix D was estimated from the change in the level of BDT #4 as it was emptied and the corresponding percent of the total tank capacity that this change represented of BDT #4 that was emptied. Outlet flow measurement was not required in the calculations for emission rates. The inlet flow measurements were used for the material balance

calculations assuming that the same amount of latex exited the BDT as was put into the tank.

6.1.2.2 Temperature Measurements. The temperature of the latex sample at the inlet and outlet were taken from direct readouts with a metal thermometer. The thermometer was placed in the sample jar while the sample was being obtained.

6.1.2.3 Latex Sampling Procedures. The inlet latex sampling was coordinated with the process engineer to obtain the timing of the reactors' releasing into the blowdown tank. The reactors were monitored for the valve to BDT #4 to open. The sample was taken 5 minutes after the valve opened. The sample was taken from the product sample valve at the bottom of the reactor. This valve was opened, and the latex was allowed to flow at a constant rate into a bucket for approximately 30 seconds. The latex was then obtained and prepared according to the latex sampling procedures in Appendix H.

The outlet latex sampling was coordinated with the plant process engineer to obtain the timing of BDT #4 emptying its contents to the shaker screens. The sample was taken approximately 5 minutes after the valve had been opened to process the BDT #4 latex to the shaker screens. The sample was obtained from a product sampling valve. The latex was purged from the sample valve, obtained, and prepared the same as the inlet latex sample.

6.1.4 Central Vacuum System Sampling Procedures

The central vacuum system exhaust sample location was labeled #1, and sample position 1A was a portion of this gas stream. The gas stream at #1 was the gas concentration emitted to the atmosphere from the blow down process and other processes which were exhausted from the central vacuum system.

6.1.3.1 Flow Measurements. The flow measurements at the central vacuum system outlet were determined with an orifice placed in-line between the central vacuum system and the stack outlet to the atmosphere. The orifice was installed by plant personnel according to manufacturer's specifications (see Section 5.2.1). A 0"-10" of water magnehelic was installed in line with the D_p cell to allow for the monitoring of the low flows.

6.1.3.2 Temperature Measurements. The temperature of the outlet gas stream from the central vacuum system was monitored during the sampling period using a K-type thermocouple wire attached to a Digimite temperature display.

6.1.3.3 Gas Sampling Procedure. Integrated gas samples and continuous monitoring of the hydrocarbon level were obtained at the central vacuum system outlet. The evacuated can system was required for the integrated gas sample according to the modified EPA Method 110 described in Appendix H. The Horiba OPE-405 hydrocarbon analyzer was utilized as the continuous monitoring of the outlet stream. The Horiba OPE-405 utilizes the flame ionization detection method of analysis and was operated according to the procedures in Appendix H. The timing of the sampling was simultaneously with the blowdown tank outlet.

6.1.4 Shaker Screen Exhaust Sampling Procedure

This sample location was labeled position 6. This sample location was the fugitive gaseous emissions escaping from the process of filtering the latex through the shaker screens. A three tool metal probe was added to the sample probe for maintaining the sample point in the center of the shaker screen.

6.1.4.1 Flow Measurements. No flow measurements were obtained from the shaker screen emission.

6.1.4.2 Temperature Measurements. The temperature of the gas stream being sampled was monitored with a K-type thermocouple wire connected into a Digimite[®] temperature display. The point monitored was at the sample point by securing the thermocouple to the sample probe.

6.1.4.3 Gas Sampling Procedure. An integrated gas sample was obtained during the shaker screen operation. The evacuated can system was required to obtain the sample according to the modified EPA Method 110 presented in Appendix H.

6.1.5 Steam Stripper Vacuum System Outlet

This sample location was labeled position 2 and was the gas emissions from the stripper system. This location was monitored during a period when the steam stripper was operating.

6.1.5.1 Flow Measurements. The flow measurement at the steam stripper outlet were monitored with a vane anemometer. The anemometer was installed in the gas stream by modifying the outlet vent with flexible hosing (see Figure 5-12). The flow through the anemometer was recorded during the test period.

6.1.5.2 Temperature Measurements. The temperature measurements were obtained with a K-type thermocouple wire connected into a Digimite[®] temperature readout. The thermocouple was placed in the gas stream flow through a port at the end of the modified outlet vent (flexible hose).

6.1.5.3 Gas Sampling Procedures. Integrated gas samples and continuous HC monitoring were obtained at the styrene stripper outlet. The integrated gas sample was obtained with an evacuated can sampling system according to the modified EPA Method 110 as described in Appendix H. The continuous monitoring was with a Horiba OPE-405 hydrocarbon analyzer. This instrument uses the flame ionization detection method of HC analyses and was operated according to the procedures in Appendix H.

6.1.6 Steam Stripper Inlet and Outlet Latex Sampling

The inlet latex flow to the stripper was labeled sample position 8, and the outlet latex flow was labeled position 9. The samples were obtained simultaneously and taken during the sampling of the outlet gaseous emissions from the steam stripper.

6.1.6.1 Flow Measurements. The flow measurement for the latex stream feeding through the steam stripper was monitored on a GPM meter by the plant personnel. This feed rate was recorded and utilized for the inlet and outlet latex flow.

6.1.6.2 Temperature Measurements. The temperature of the latex sample at the inlet and outlet were taken from direct readouts with a metal thermometer. The thermometer was placed in the sample jar and monitored while the was being taken.

6.1.6.3 Latex Sampling Procedures. The outlet latex sample was taken directly from a sample production valve according to the latex sampling procedure described in Appendix H. But a modification of this latex sampling procedures was required at the inlet. The inlet latex

sample was taken from an open tank feeding into the stripper. The latex sample was obtained by dipping the sample jar into this tank.

Precautions were taken to obtain the sample from the center of the tank and below the hardened layer of latex to ensure a representative sample.

6.1.7 Storage Tank Vent

The sample location at the storage tank vent was labelled position 11. The sample timing was coordinated with the steam stripper gas outlet sample and the operation of filling the storage tank.

6.1.7.1 Flow Measurements. The flow measurements were obtained with a vane anemometer installed in the tank vent. The flow through the anemometer was monitored during testing.

6.1.7.2 Temperature Measurement. The temperature measurements were obtained with a K-type thermocouple wire connected into a Digimite[®] temperature readout. The temperature was monitored at the sample point by securing the thermocouple to the sample probe.

6.1.7.3 Gas Sampling Procedures. An integrated gas sample was obtained during the filling of the storage tank. The evacuated can system was required in obtaining the sample according to the modified EPA Method 110 as presented in Appendix H.

6.2 ANALYTICAL PROCEDURES

There were two types of samples analyzed by GC/FID: integrated gas bag analyses and latex grab analyses. Since each type required special handling and preparation a brief discussion of the methods and any deviations from the methods are described below.

6.2.1 Analysis of Each Gas (Bag) Samples

Each gas (bag) sample was analyzed on-site, normally within thirty minutes of collection. Prior to the field program, gas samples were to be analyzed using two column types; 6' by 1/8 inch stainless steel packed with AT-1200 Bentone 34 for the determination of benzene, toluene, ethylbenzene, xylene, and styrene, and a Poropak Q column for butadiene and C₁-C₆ hydrocarbons. Due to the high concentrations of butadiene relative to C₁-C₆ hydrocarbons, the Poropak Q portion of the gas chromatographic analysis was dropped. Subsequent gas analysis was performed in the differential mode with two instruments (Shimadzu Mini I

and Shimadzu Mini II) with dual AT-1200 Bentone 34 columns. Figure 6-1 shows the flow line and valve sequence applicable to both the Shimadzu Mini 1 and Mini 2. Gas samples were flushed through a 1 ml sample loop at 0.6 lpm for 30 seconds, allowed to equilibrate, and injected in the column. Figure 6-2 shows the gas sampling system used for all heat samples. Analysis time was approximately 15 minutes per gas sample injection. Quantitation was by appropriate response factors with integration by two Shimadzu-CRIA chromatopaks.[®] A third Shimadzu gas chromatograph equipped with a conductivity detector, and molecular sieve 5A and silica gel columns, was used to quantify stationary gases.

The analysis of the gas samples indicated a saturation effect of the FID detectors when more than 5% total hydrocarbons were injected into the gas chromatograph. An alteration in the standard analytical procedure was required due to the high concentration of butadiene. This required two separate analyses on each sample. The first analysis required an injection of the neat sample to determine the concentrations of the components excluding butadiene. The second analysis required dilution of the butadiene sample to prevent saturation of the detector. The identified and quantified compounds of the first injection were utilized as internal standards to determine the dilution ratio for butadiene.

6.2.2 Analysis of Latex Samples

Latex samples were analyzed by GC/FID using an AT-1200 Bentone 34 column and undecane as an internal standard. The residual styrene in latex was stabilized using TBC in methylene chloride solution. One change in procedure was implemented on-site. The EPA Method for Determination of Residual Styrene recommends that a 50 ml aliquot of latex be dissolved in 150 ml of TBC/MeCl solution. The field samples were insoluble. A series of extractions demonstrated that three methylene chloride extractions would remove 95 percent of the residual styrene. In addition, an initial saturation period of greater than 8 hours with the first extraction was found to be beneficial. Therefore, 100 ml of TBC/MeCl solution was added to each latex sample (50 ml), sealed, and allowed to stand up to 8 hours. The methylene

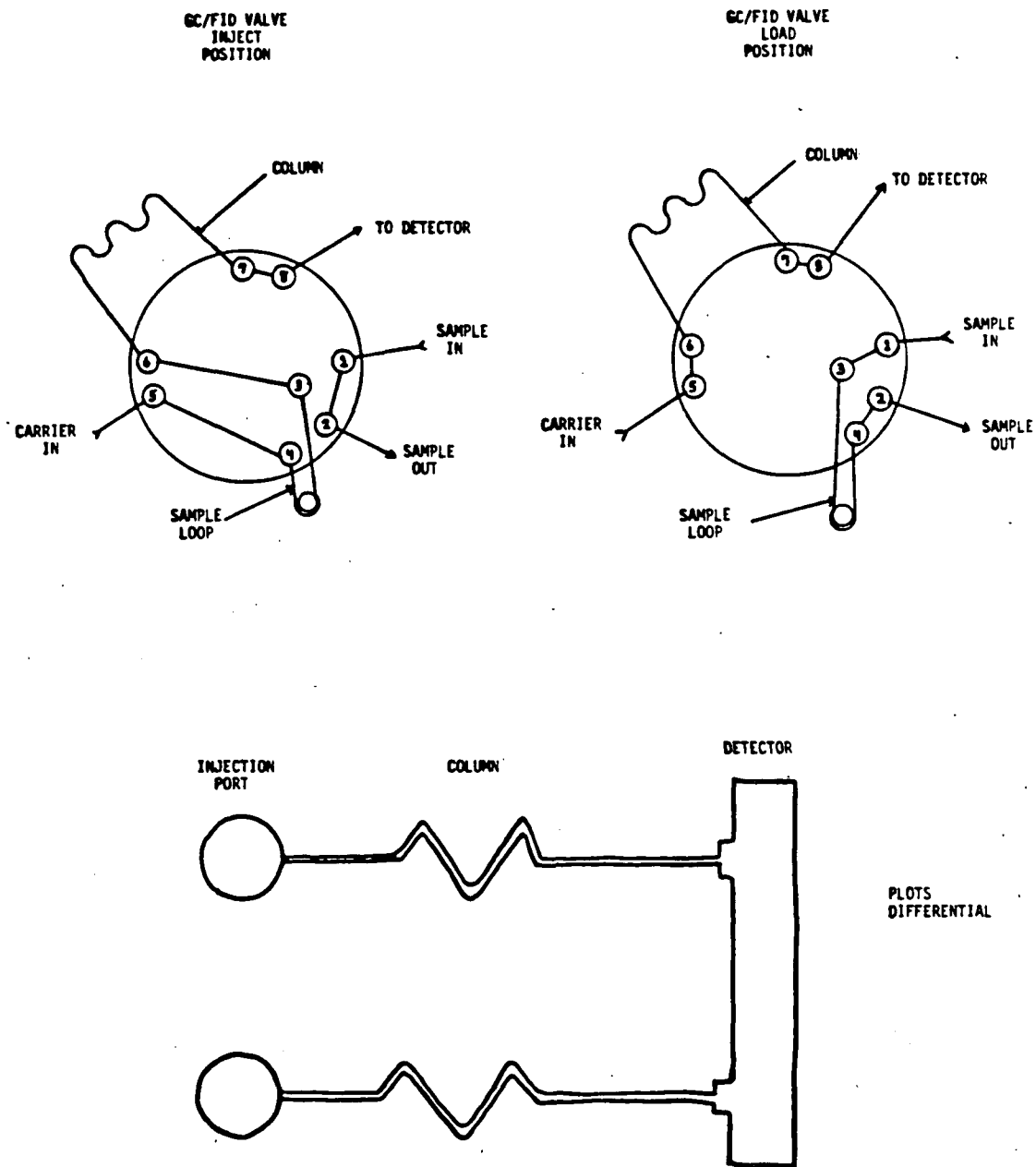


Figure 6-1. Flow Line

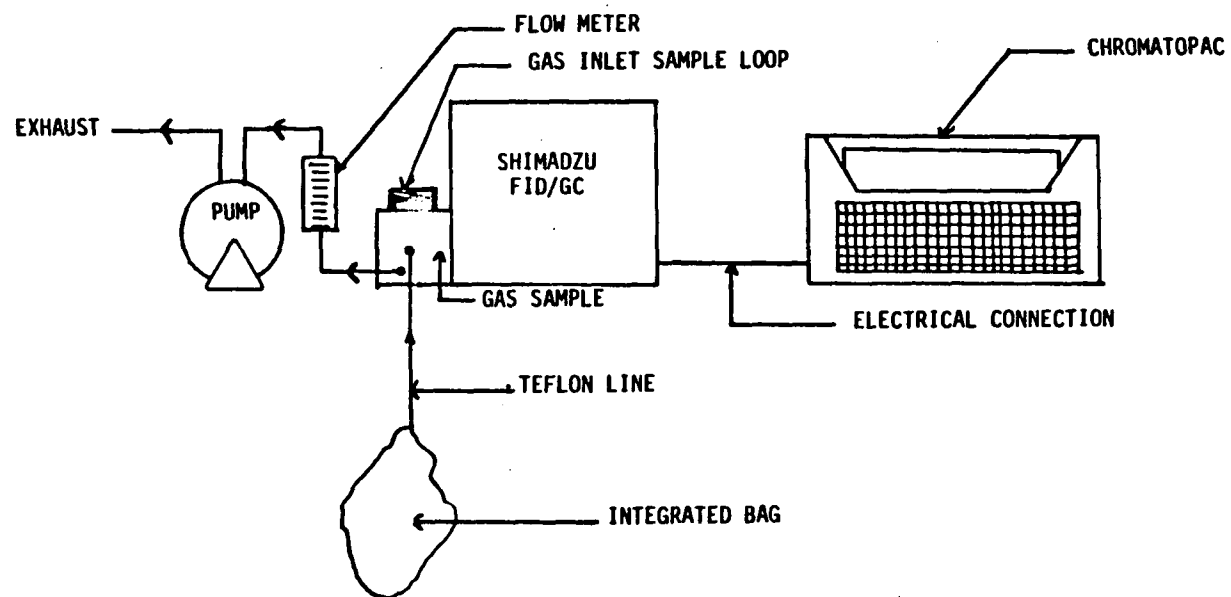


Figure 6-2. GC/FID Gas Sampling System

chloride (MeCl) was decanted and followed with two additional extractions of 100 ml each to complete the extraction. Both the second and third extractions required the addition of 100 ml of TBC/MeCl, extraction of the latex for 10 minutes, and the combination of the extraction volume with the previous one. The total extraction volume was 300 milliliters.

6.3 CONTINUOUS MONITORING AT THE BLOWDOWN TANK OUTLET, CENTRAL VACUUM SYSTEM OUTLET, AND STYRENE STRIPPER VACUUM OUTLET WITH A FLAME IONIZATION DETECTOR

A Horiba OPE-405 hydrocarbon analyzer was utilized as the continuous monitor at the blowdown tank outlet, central vacuum system outlet, and styrene stripper vacuum outlet. The instrument was set up at each position on separate tests day and operated according to the Horiba Operational Manual. The FID was calibrated with standard gases on a propane basis. Therefore, the FID results are given in total hydrocarbons as propane. The following sections explain the FID results from the test day at the particular location and compare the results to the plant process and integrated bag results.

6.3.1 Continuous Monitor by FID at the Blowdown Tank Outlet (March 27, 1980)

Figure 6-3 shows a comparison between the plant process, the FID, which was set up at the blowdown outlet and gave a reading of THC as propane, and the bag samples which were analyzed by compound as propane. During each reactor dump into the blowdown tank, the FID showed high peak readings between 18 and 24×10^4 ppm THC. During most of the degassing period, no FID data was obtained due to failure of the sample pump. It can be seen toward the end of the degassing that the THC concentration decreased to between 2×10^4 and 10×10^4 ppm THC. The bag samples represented averages taken throughout the day. The compound of the highest concentration was butadiene which ranged from 2.7 to 11.2×10^4 ppm. Styrene was the next highest, ranging from 0.11 to 0.60×10^4 ppm. The concentration of each bag corresponded to be average FID reading during the same time frame.

6.3.2 Continuous Monitor by FID at the Central Vacuum System Outlet (March 31, 1980)

Figure 6-4 shows a comparison between the plant process and the FID which was set up at the central vacuum system. No bag samples were

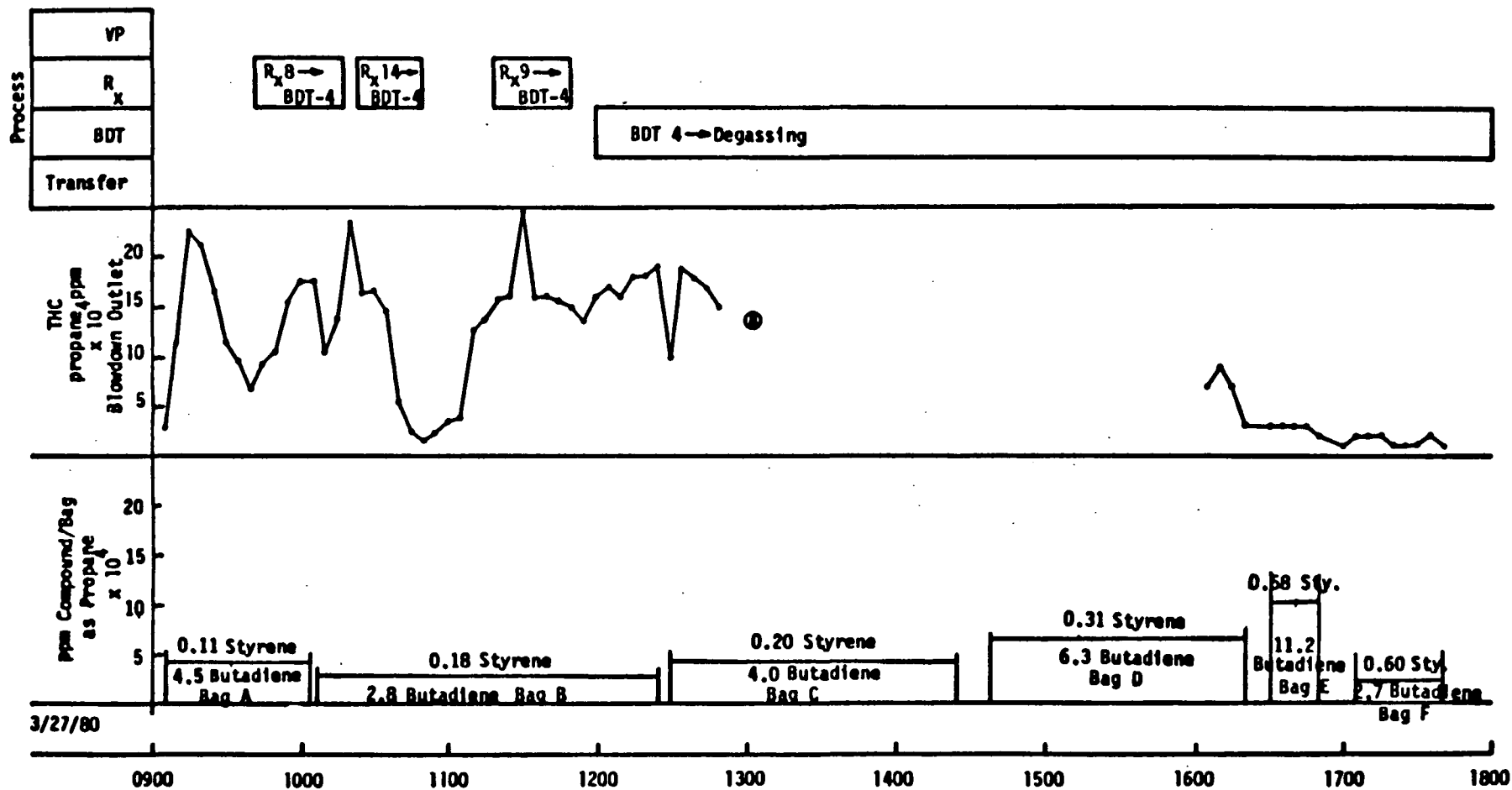


Figure 6-3. FID Results at the Blowdown Tank Outlet on March 27, 1980

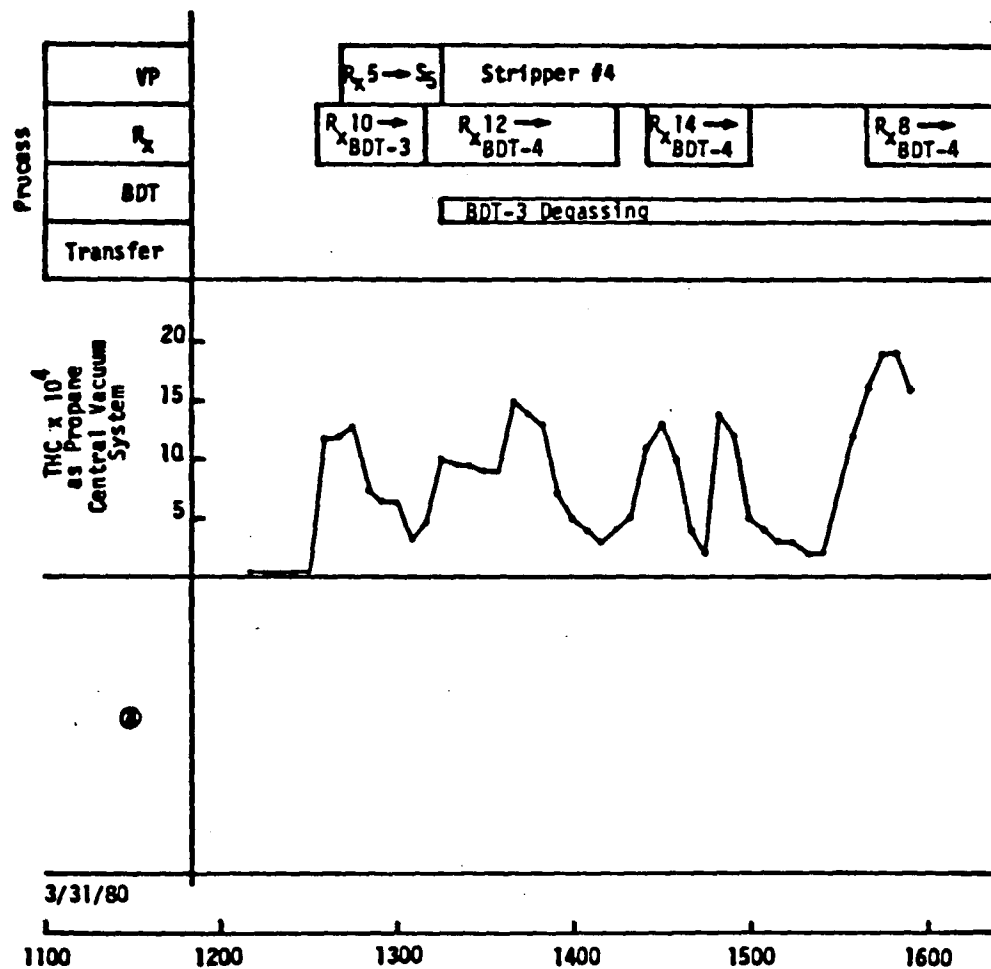
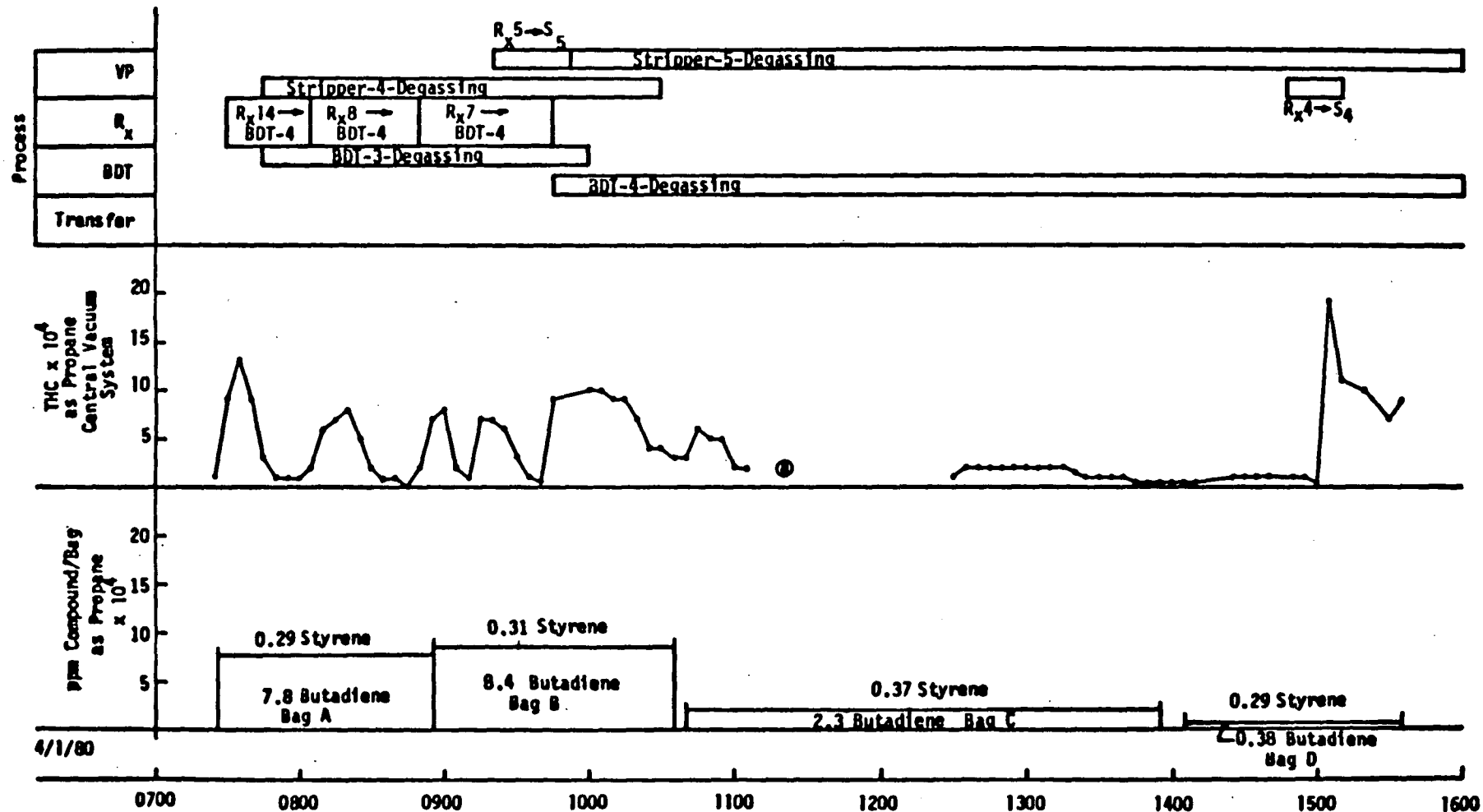
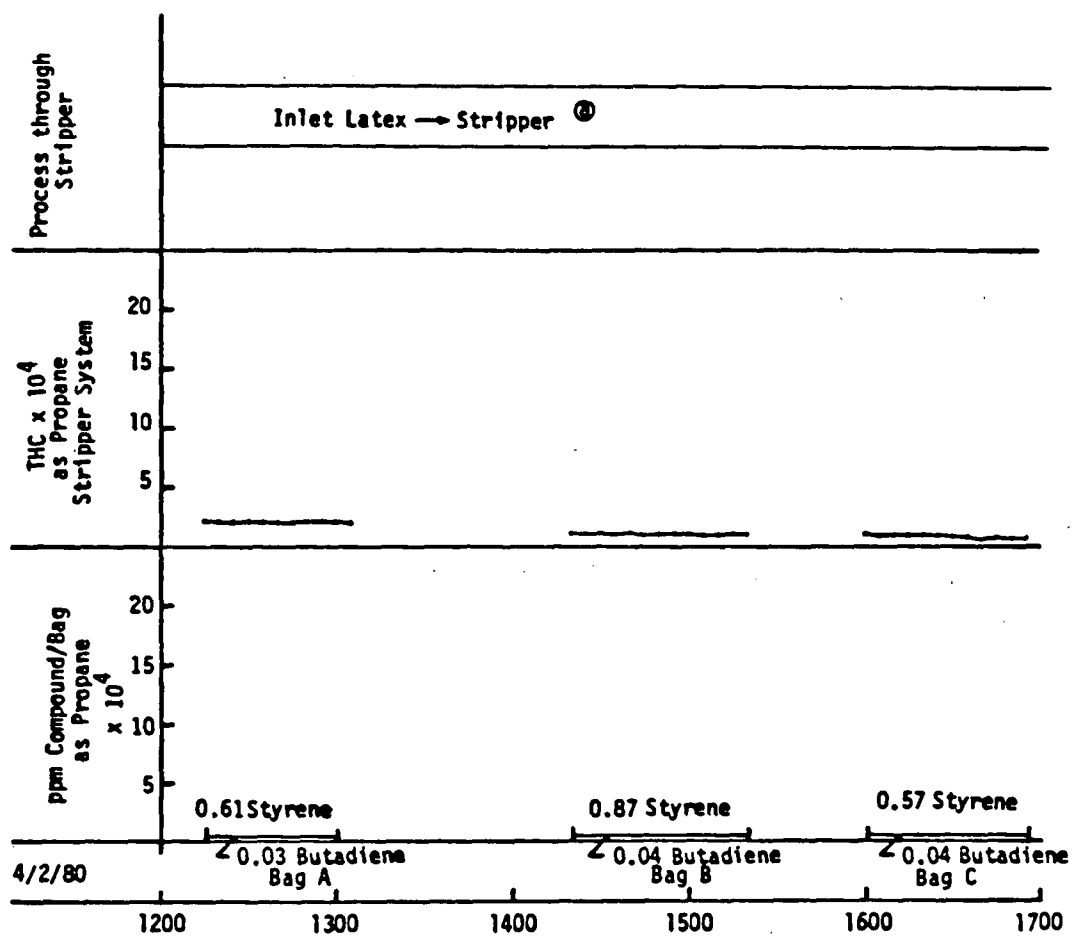


Figure 6-4. FID Results at the Central Vacuum System Outlet on March 31, 1980



⊗ No FID data obtained.

Figure 6-5. FID Results at the Central Vacuum System Outlet on April 1, 1980



② Inlet latex feed stream remained constant during test period.

Figure 6-6. FID Results at the Styrene Stripper Outlet on April 2, 1980

taken at this location on this day. (Prior to the reactor dumps the FID showed readings between 1×10^4 ppm and 2×10^4 ppm THC as propane.) During each reactor dump into the blowdown tanks, the FID showed high peak readings between 13×10^4 and 18×10^4 ppm THC as propane. The effects of the degassing process could be seen only inbetween the reactor dumps due to the low concentration of the emissions, which were between 2 and 4×10^4 ppm THC as propane.

6.3.3 Continuous Monitor by FID at the Central Vacuum System Outlet (April 1, 1980)

Figure 6-5 shows a comparison between the plant process, the FID which was set up at the central vacuum system, and the bag samples. During each reactor dump into the blowdown tank the FID showed high peak readings between 7 and 14×10^4 ppm THC as propane. Butadiene was the component with the highest concentration averaging 8.1×10^4 ppm as propane during this reactor blowdown period. Styrene had a concentration averaging 0.30×10^4 ppm as propane. The FID readings decreased during the degassing period to less than 5×10^4 ppm. During this time the butadiene concentration in the bag decreased to 2.3×10^4 ppm. During the last reactor dump the FID showed a peak of 18×10^4 ppm, then continued to decrease as the degassing process continued.

6.3.4 Continuous Monitor by FID at the Styrene Stripper Outlet (April 2, 1980)

Figure 6-6 shows a comparison between the FID which was set up at the stripper system and the bag samples that were collected. The FID showed concentrations between 1.0×10^4 and 3×10^4 ppm THC as propane. According to the analysis of the bag samples, the compound with the highest concentration was styrene which ranged from 0.67 to 0.87×10^4 ppm as propane, butadiene ranged from 0.03 to 0.04×10^4 ppm as propane.

6.4 QUALITY ASSURANCE AND QUALITY CONTROL

Attaining the necessary results required specialized analytical techniques and considerations. Therefore, this section was divided into three subsections to discuss each procedure in depth. The three subsections are:

6.4.1 CALIBRATION

6.4.2 DEGRADATION STUDIES

6.4.3 AUDIT SAMPLES

6.4.1 Calibration

The daily calibration procedure followed throughout the field testing consisted of an instrument warm-up of thirty minutes followed by area integration of known benzene and butadiene gas standards and area integration of a liquid standard containing 1% styrene and 1% undecane. Replicate standard injections were made with a deviation in the area counts of less than 5%. Standards were injected during analysis to assess the stability of the instrument response. Gaseous standards were injected in the same manner as gaseous samples (i.e., the sample loop was flushed with gas at a rate of .5 liter per min. for thirty seconds.) From the area counts and the concentration of the standard, a response factor was calculated daily and applied to the area counts of the compounds of interest in the samples to determine concentration in ppm (Appendix B). Prior to any sample analysis, the instruments were calibrated with a 1300 ppm butadiene standard and a 98.1 ppm benzene standard.

The liquid standard used in this test was 1% styrene and 1% undecane in methylene chloride TBC solution. One μ l injection was made into the GC/FID and the area counts of undecane and styrene recorded until they were reproducible to within 5%. A response factor for styrene was calculated from the area counts and concentration of styrene in ppm. An average area count was determined for the undecane internal standard.

Linearity of the instruments was determined for both benzene and styrene. Benzene gas standards with ppm concentrations of 82, 106, and 495 were used in the analyses (see Figure 6-7) with calculations of mean and standard deviation included. Liquid styrene standards were prepared with percent concentrations of 0.1, 0.25, and 1.0. Figure 6-8 shows the linearity of the instrument, with the mean and standard deviation calculations included.

6.4.2 Degradation Studies

Degradation rates were not obtained from the original presurvey samples due to the time delay of days between the sampling and the

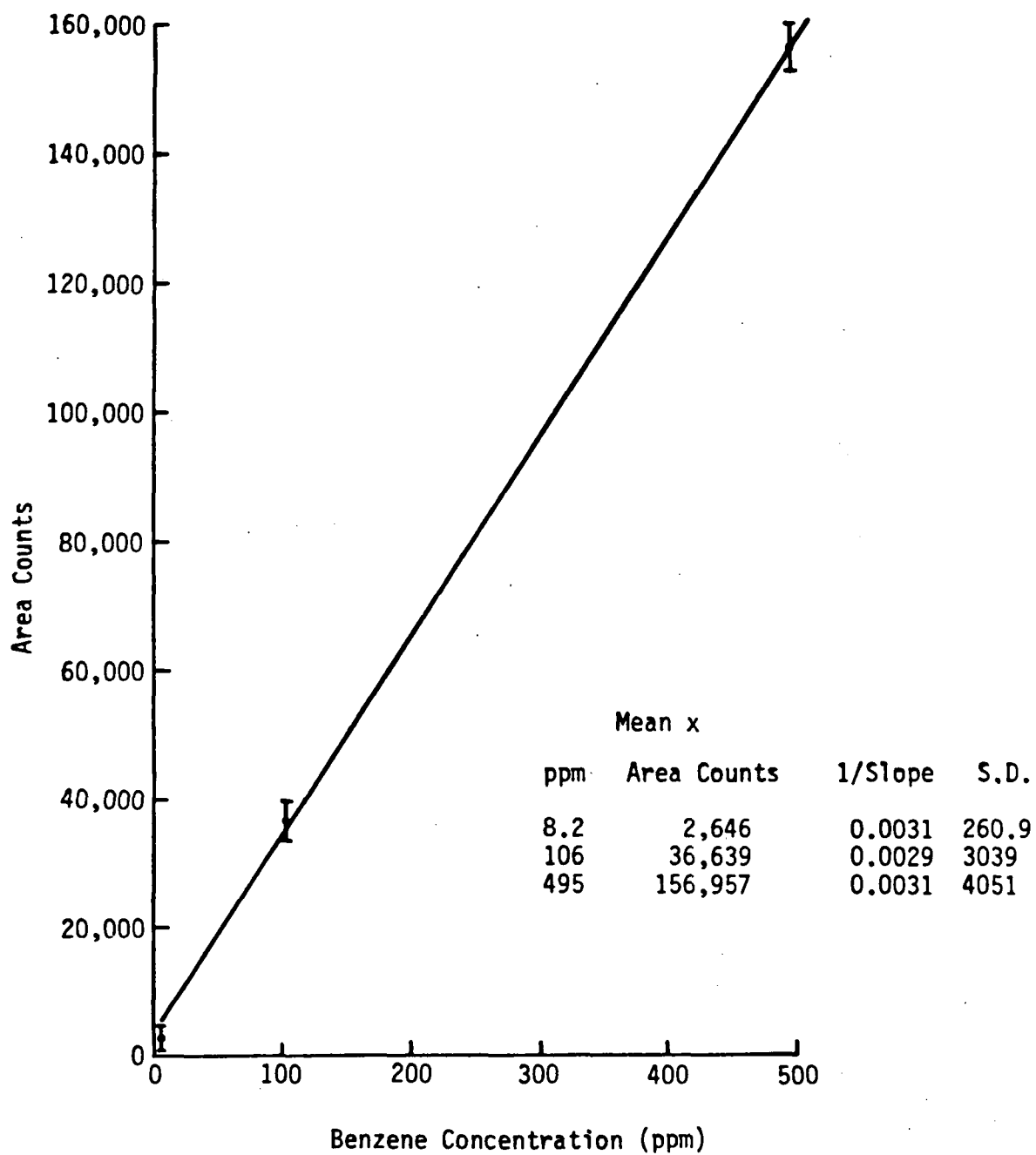


Figure 6-7. Instrument Linearity for Benzene

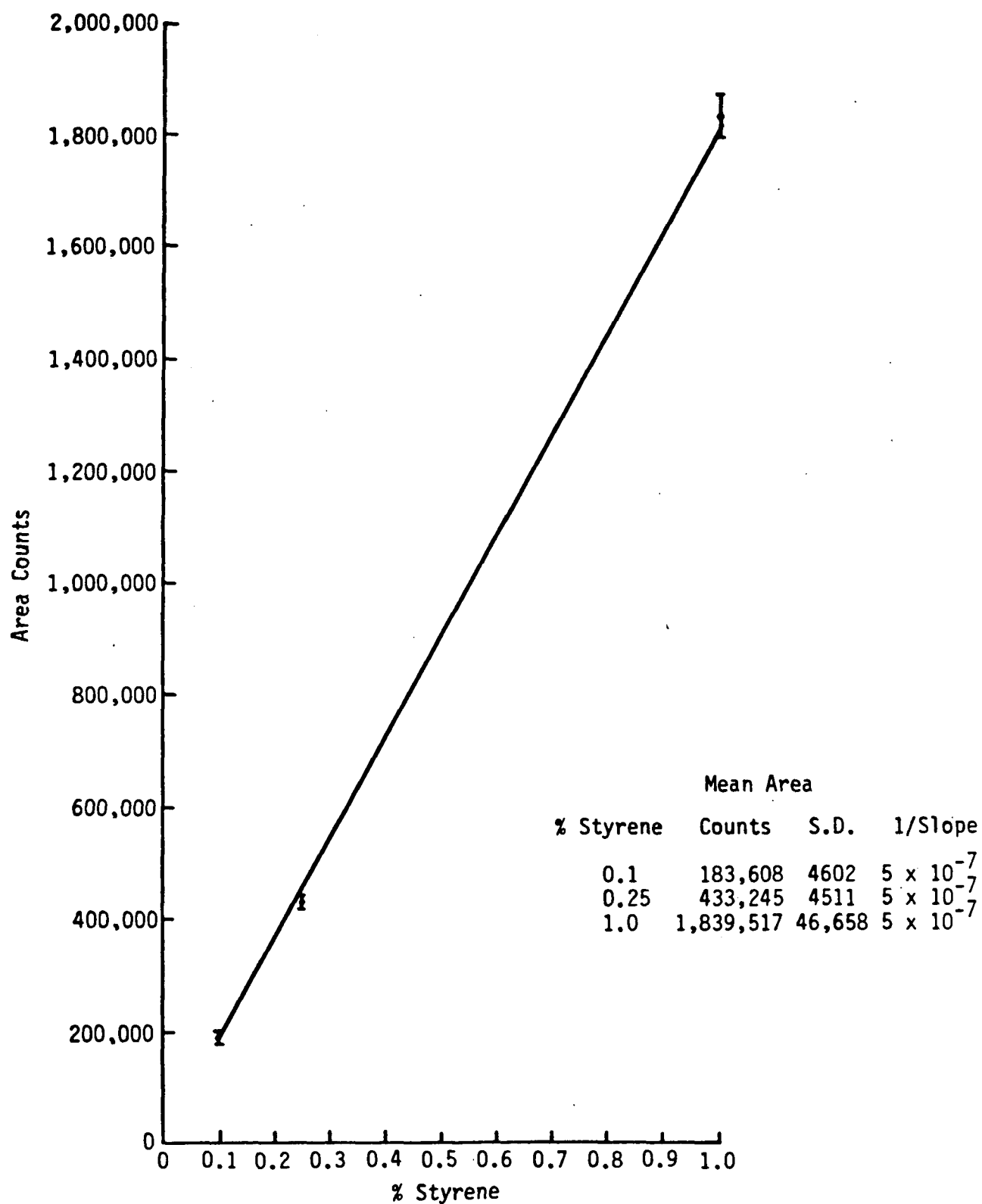


Figure 6-8. Instrument Linearity for Styrene

initial analysis. Previous observations of the degradation behavior in bags indicated the necessity of this type of study. TRW had confirmed that degradation of gaseous hydrocarbon samples was severe and substance specific. For example, a sample containing benzene, styrene, and other hydrocarbons exhibit a 15% loss of benzene in 48 hours and a 65% loss of styrene over the same time period. Hydrocarbons whose retention times fall between benzene and styrene exhibit similar losses.

Another related consideration involves the temperature differential affecting the sample between the 120°F stack and ambient conditions in the field lab. The temperature effects were investigated at the field site by initial analysis of a heated bag sample (~100°F) and repeated analysis over a four-hour period. The time between collection and analysis, not temperature, proved to be the major consideration. Although the degradation, or loss of butadiene and benzene (<10%) was acceptable, the percent loss for molecules with a carbon number of C₇ and greater ranged from 15 to 59%. The degradation loss is shown in Figures 6-9 to 6-12. Based upon the degradation study, all bag samples during the test were analyzed within 1 hour of collection. In most cases, analysis was within thirty minutes of collection.

Preliminary investigation of the latex samples indicated that styrene in methylene chloride solutions containing 4-tertiary butylpyrocatechol (TBC) would remain constant over a 3-day period. Initial field analyses required the determination of stability of styrene in methylene chloride containing TBC. This was demonstrated by the repeated analysis of two latex samples over a period of 9 days with a degradation of less than 2 percent (Figure 5-6). Based upon these observations, latex samples were analyzed within 9 days of sampling.

6.5 AUDIT SAMPLES

EPA supplied three gas samples of unknown compounds and concentrations. The audit samples were analyzed after the daily calibration procedures (Section 6.1) in the same manner as all the gas samples. The compounds were identified by their retention times, and the concentrations were calculated from the daily response factors (Table A-10).

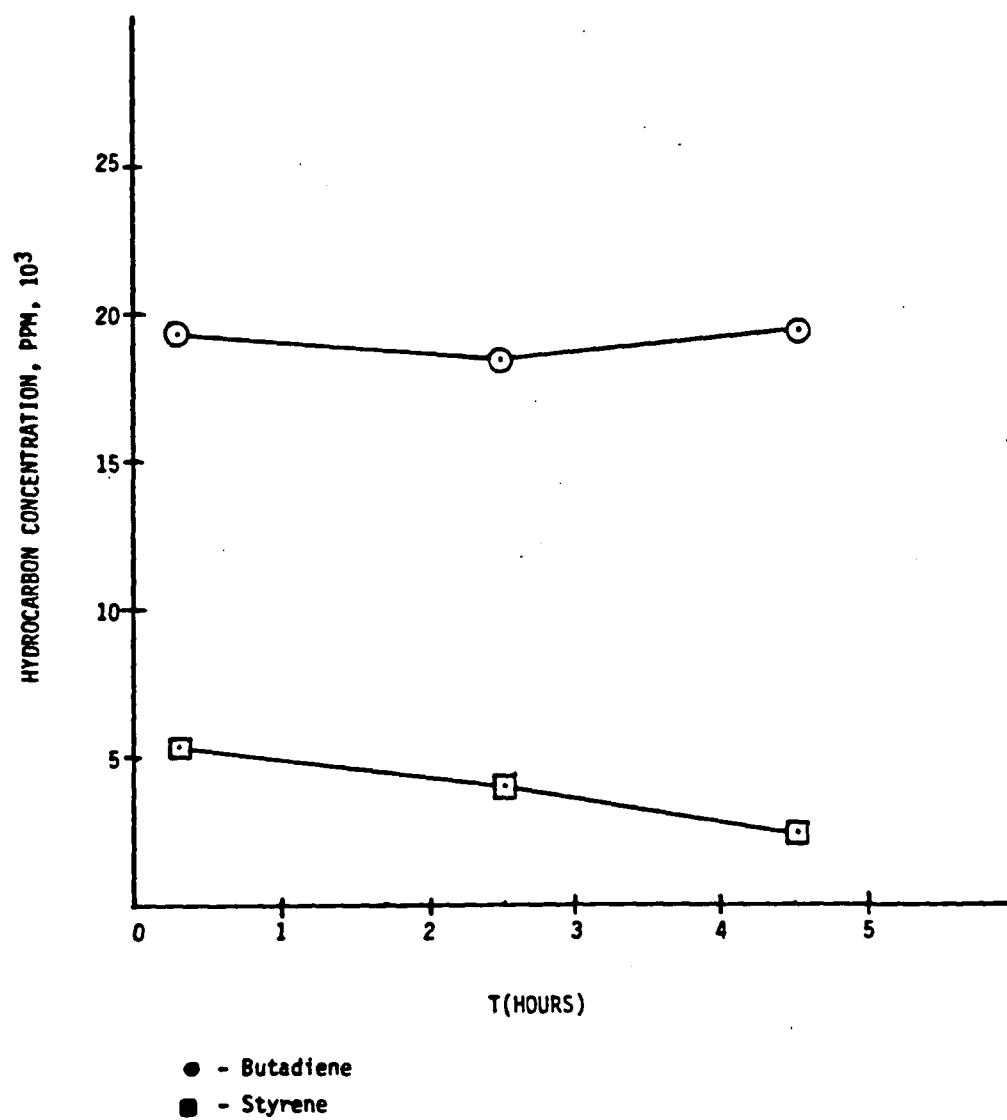


Figure 6-9. Degradation Study - Hydrocarbons -
Bag Sample - Mogadore, Ohio

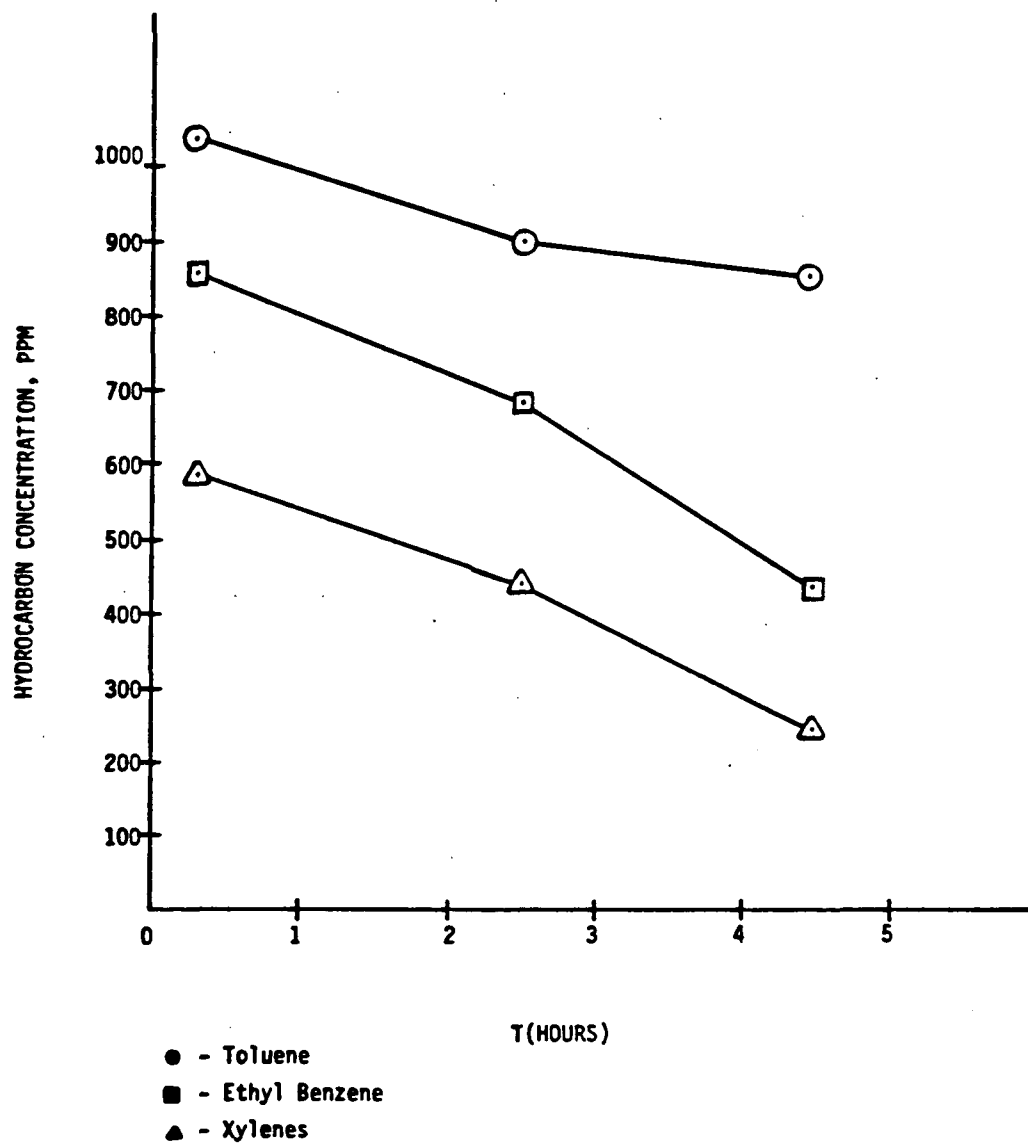


Figure 6-10. Degradation Study - Hydrocarbons -
Bag Sample - Mogadore, Ohio

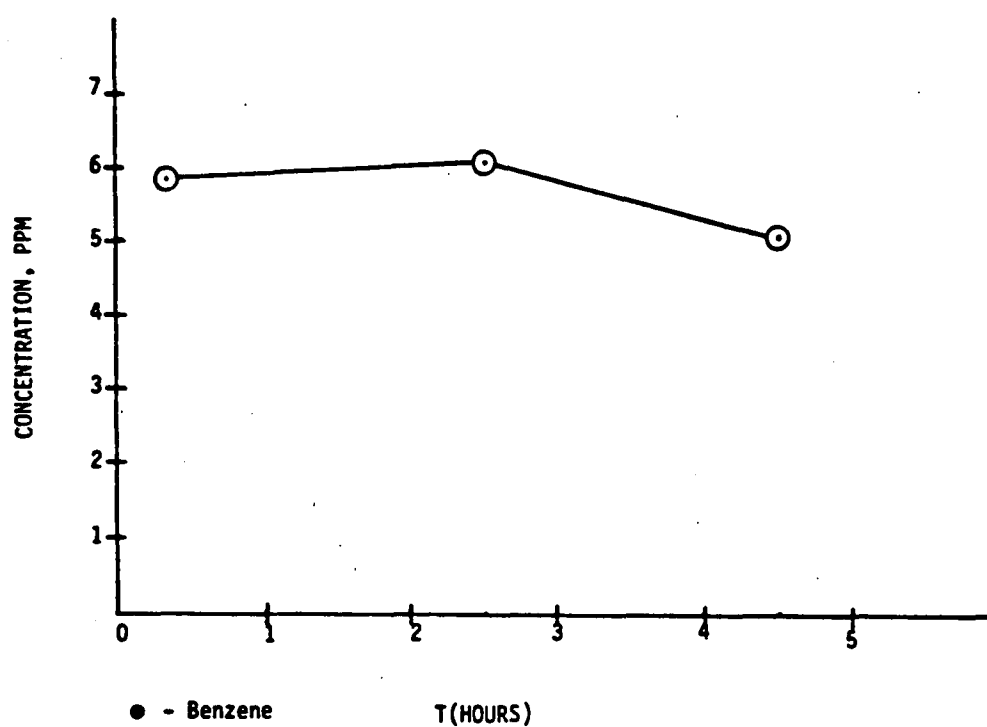


Figure 6-11. Degradation Study - Benzene -
Bag Sample - Mogadore, Ohio

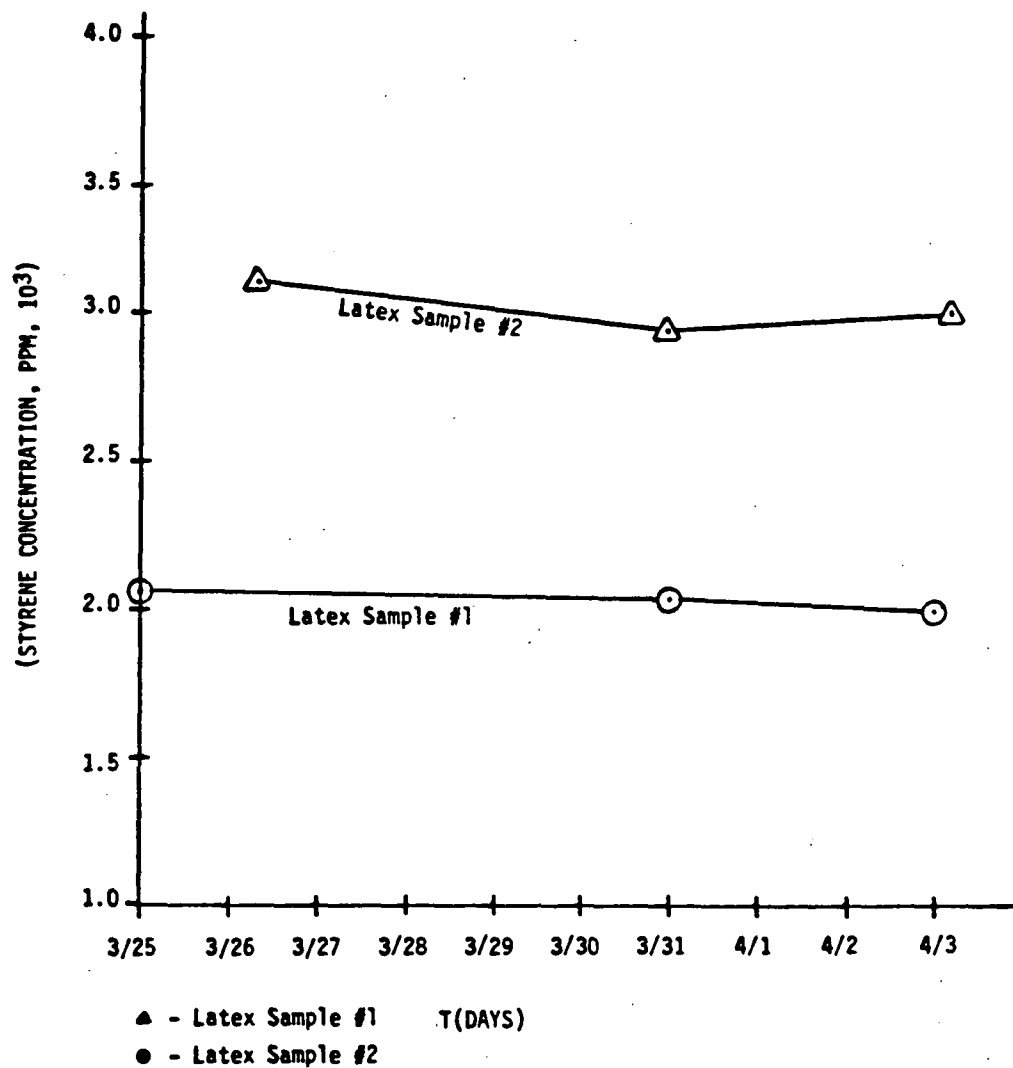


Figure 6-12. Degradation Study - Latex (Styrene) -
Mogadore, Ohio - March 25, 1980-April 3, 1980

EPA also supplied three liquid audit samples of unknown concentrations. The audit samples were extracted and analyzed as described in the latex analyses method. The concentrations were calculated from the daily response factors (Table A-10). The summary or results of the audit samples appear in Table 6-1. The most significant error occurred in the analysis of the butadiene gas audit (24% from audit valve). The reason for this deviation was probably the results of analyzing a 25 ppm level standard with an instrument calibrated with a 1300 ppm level standard. The samples collected during the test had extremely high levels of butadiene and even after dilution were closer in range of 1300 ppm than 25 ppm.

Table 6-1. AUDIT RESULTS

| Sample # | Compound | Measured (ppm) | Audit Values ^a (ppm) | % Difference ^b |
|-------------|-----------|----------------|---------------------------------|---------------------------|
| 288-BAL111 | Benzene | 344.7 | 358 | -3.7% |
| 642-B117 | Benzene | 100.8 | 106 | -4.9% |
| 1032-A10567 | Butadiene | 25.9 | 20.9 | 23.9 |
| T | Styrene | 1048 | 1000 | 4.8% |
| U | Styrene | 10261 | 10000 | 2.6% |
| V | Styrene | 4187 | 5000 | -16.3% |

^aValue supplied by project officer.

^b% difference = $\frac{\text{measured} - \text{audit}}{\text{audit}} \times 100$